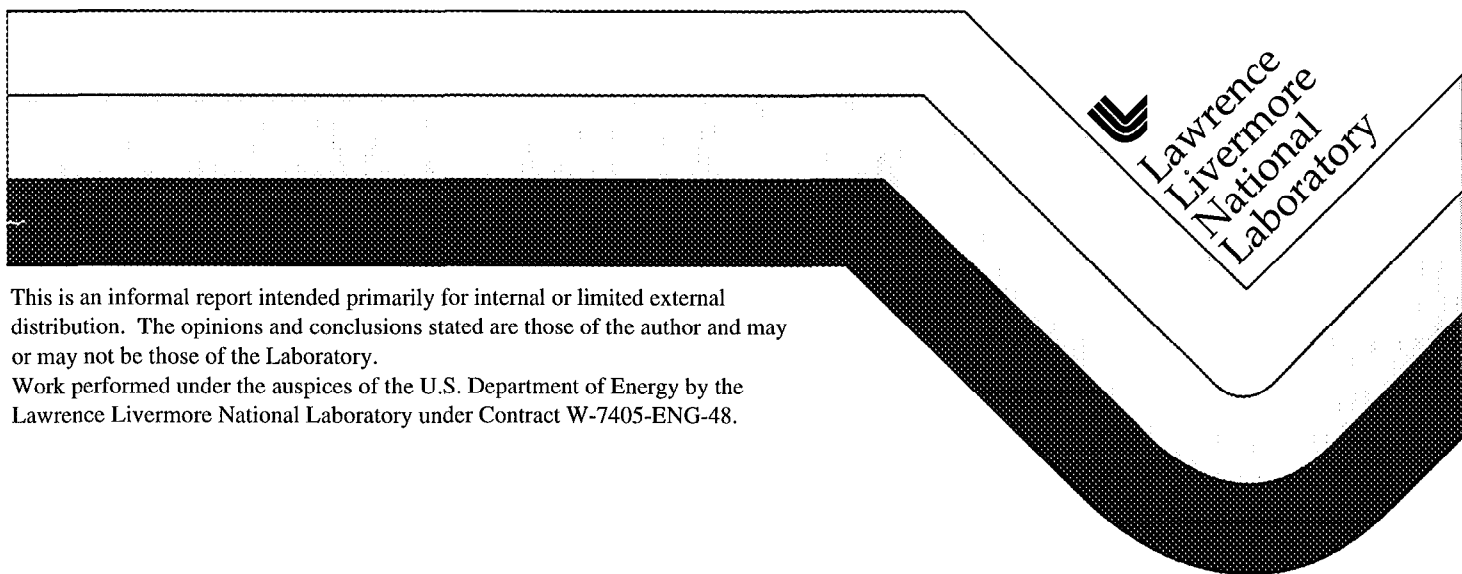


Environmental Management Science Program FY1997 Progress Report

Charles R. Carrigan
Editor

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Experimental Determination of Contaminant Metal Mobility as a Function of Temperature, Time and Solution Chemistry

Lawrence Livermore National Laboratory
September 1997

Progress Report

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Research Objective

The objective of this work is to determine the fundamental data needed to predict the behavior of Sr at temperature and time scales appropriate to thermal remediation, because ^{90}Sr is a major contaminant at Hanford and INEL sites (Duncan, 1995) and thermally-enhanced technologies used to remediate organic contaminants (Newmark and Aines, 1995) may improve the efficiency and speed of metal remediation as well.

Research Statement

Our approach combines macroscopic sorption/precipitation and desorption/dissolution kinetic experiments, which track changes in solution composition, with direct molecular characterization of Sr in the solid phase using X-ray absorption spectroscopy. These experiments will be used to identify mechanistic geochemical reactions and their thermochemical properties that will be incorporated into geochemical computer codes.

Research Progress

This report consists of three sections: **1.** Results of Sr sorption to kaolinite and goethite from pH 4 to 10 at 25, 50, and 80°C and atmospheric $\text{CO}_2(\text{g})$; **2.** Preliminary spectroscopy results; and **3.** Review of the available thermodynamic data in the Fe-Sr-Na- NO_3 - CO_2 - H_2O system.

1. Strontium sorption to goethite and kaolinite at 25, 50, and 80°C.

In our goethite and kaolinite experiments, Sr-uptake begins in solutions undersaturated with respect to strontianite (SrCO_3) and increases in more supersaturated solutions. We know that Sr-uptake is enhanced by kaolinite and goethite, because Sr is not removed from solution over the same experimental run conditions in the absence of solid phases. It is possible that ternary Sr-carbonate complexes form at the kaolinite and goethite surfaces, and that they provide the needed "seed carbonate" to precipitate strontianite. This idea builds from direct observation of multinuclear-cobalt-surface complexes on kaolinite (O'Day et al. 1994) and the formation of a mixed nickel-aluminum hydroxide during pyrophyllite dissolution and nickel-uptake (Scheidegger et al. 1996). We expect Sr-uptake to involve the formation of multinuclear- Sr-carbonate complexes because strontianite is much less soluble than $\text{Sr}(\text{OH})_2(\text{s})$. Temperature-dependence of Sr-uptake to goethite and kaolinite is minimal. This is consistent with the small (about 0.2 orders of magnitude) temperature-dependence of strontianite solubility from 25 to 80°C.

Figures 1-4 show the results of Sr sorption to goethite and kaolinite at atmospheric $\text{pCO}_2(\text{g})$ as a function of pH and temperature. In the presence of goethite, significant Sr-uptake occurs at 25, 50, and 80°C from solutions containing pH > 8 and $[\text{Sr}]_i = 10^{-7}$ to 10^{-4} M (Fig. 2 and 3). The absolute Sr-

uptake increases with increasing $[Sr]_i$ at constant temperature and at $pH > 8$.
There is a slight increase in Sr-uptake with increasing temperature for

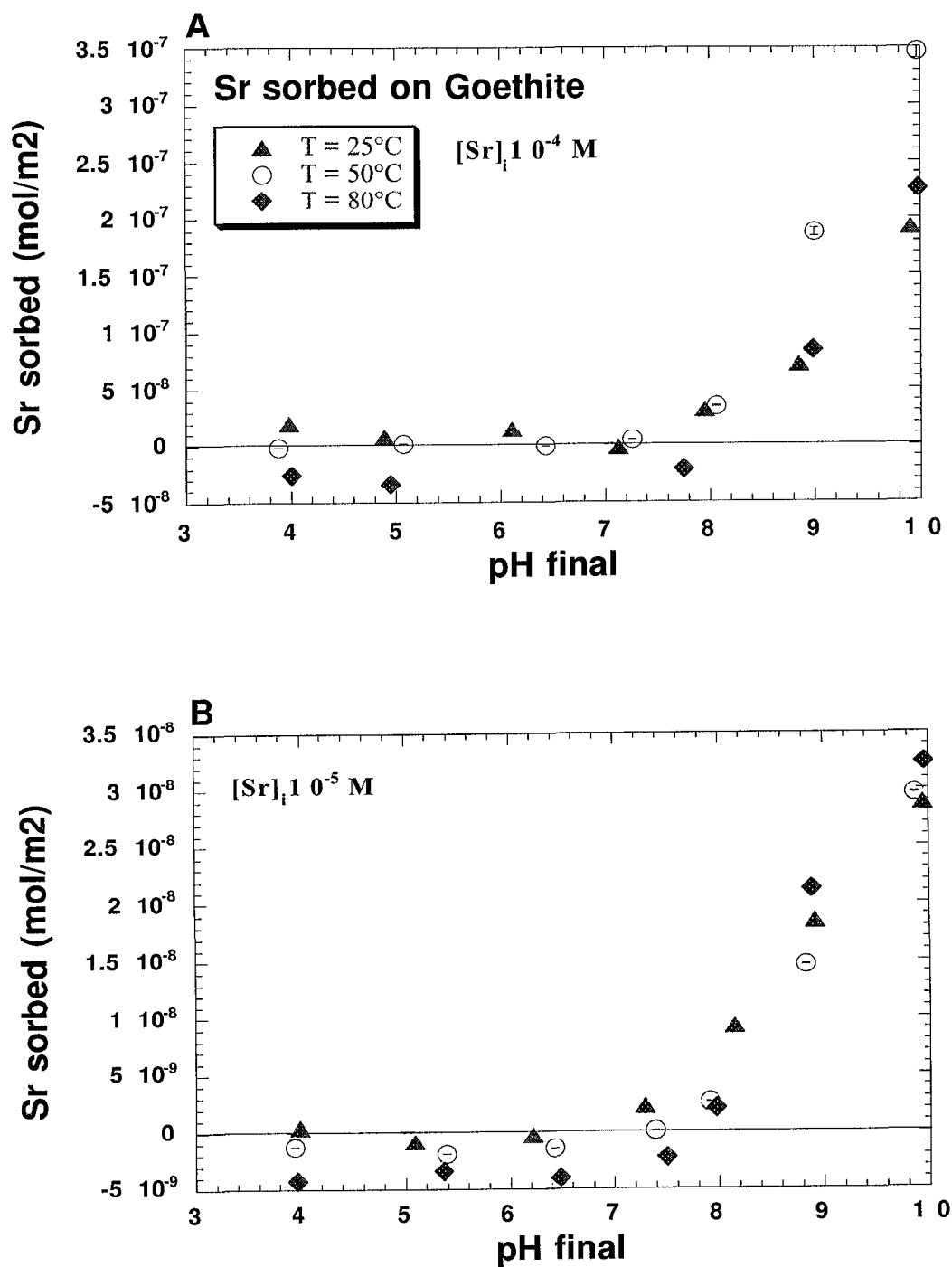


Figure 1. Strontium-uptake at goethite interface as a function of pH at 25, 50 and 80°C from solutions containing initial Sr concentrations A $[\text{Sr}]_i = 10^{-4} \text{ M}$, B $[\text{Sr}]_i = 10^{-5} \text{ M}$, C $[\text{Sr}]_i = 10^{-6} \text{ M}$, D $[\text{Sr}]_i = 10^{-7} \text{ M}$.

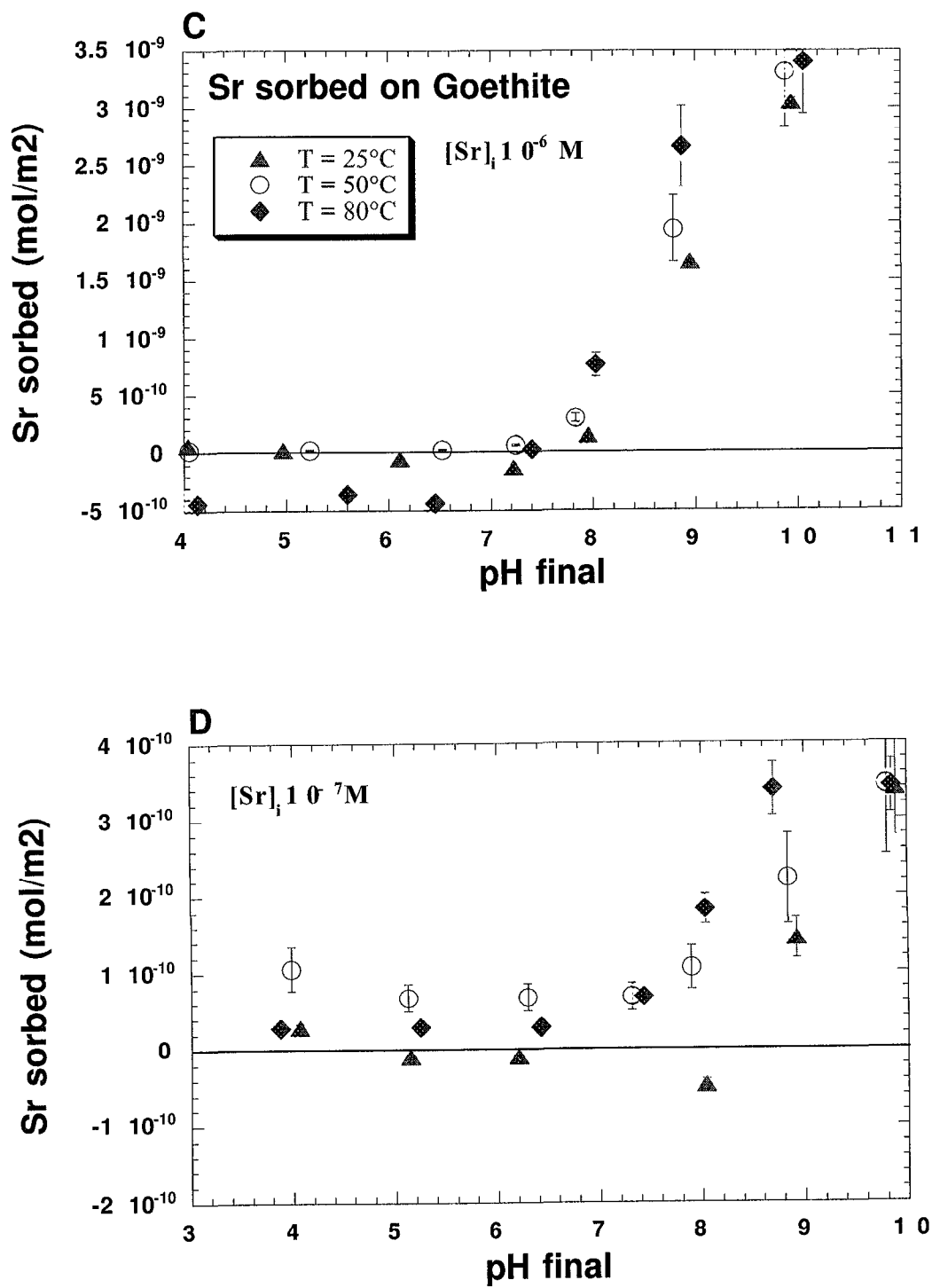


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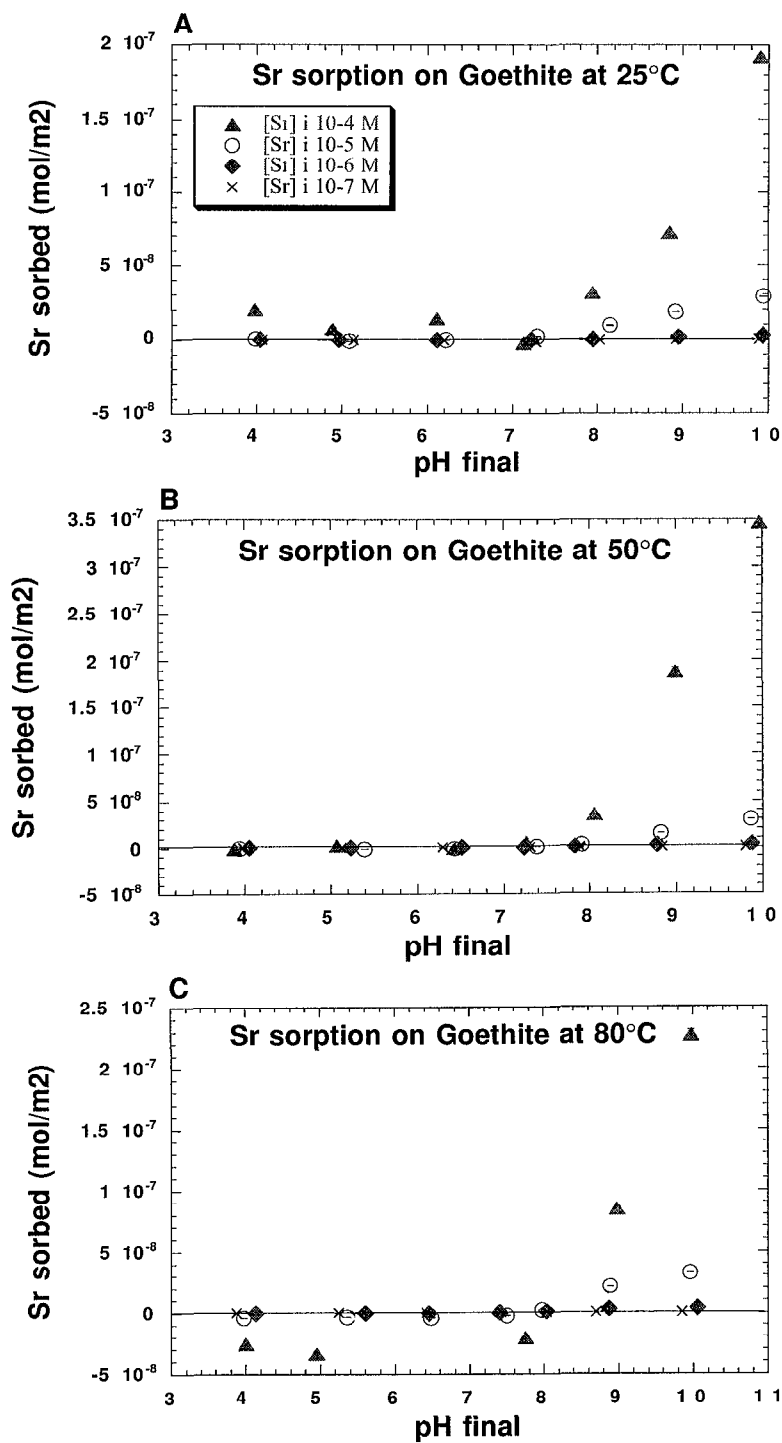


Figure 2. Strontium-uptake at goethite interface as a function of pH and initial Sr concentration at A 25°C, B 50°C, and C 80°C.

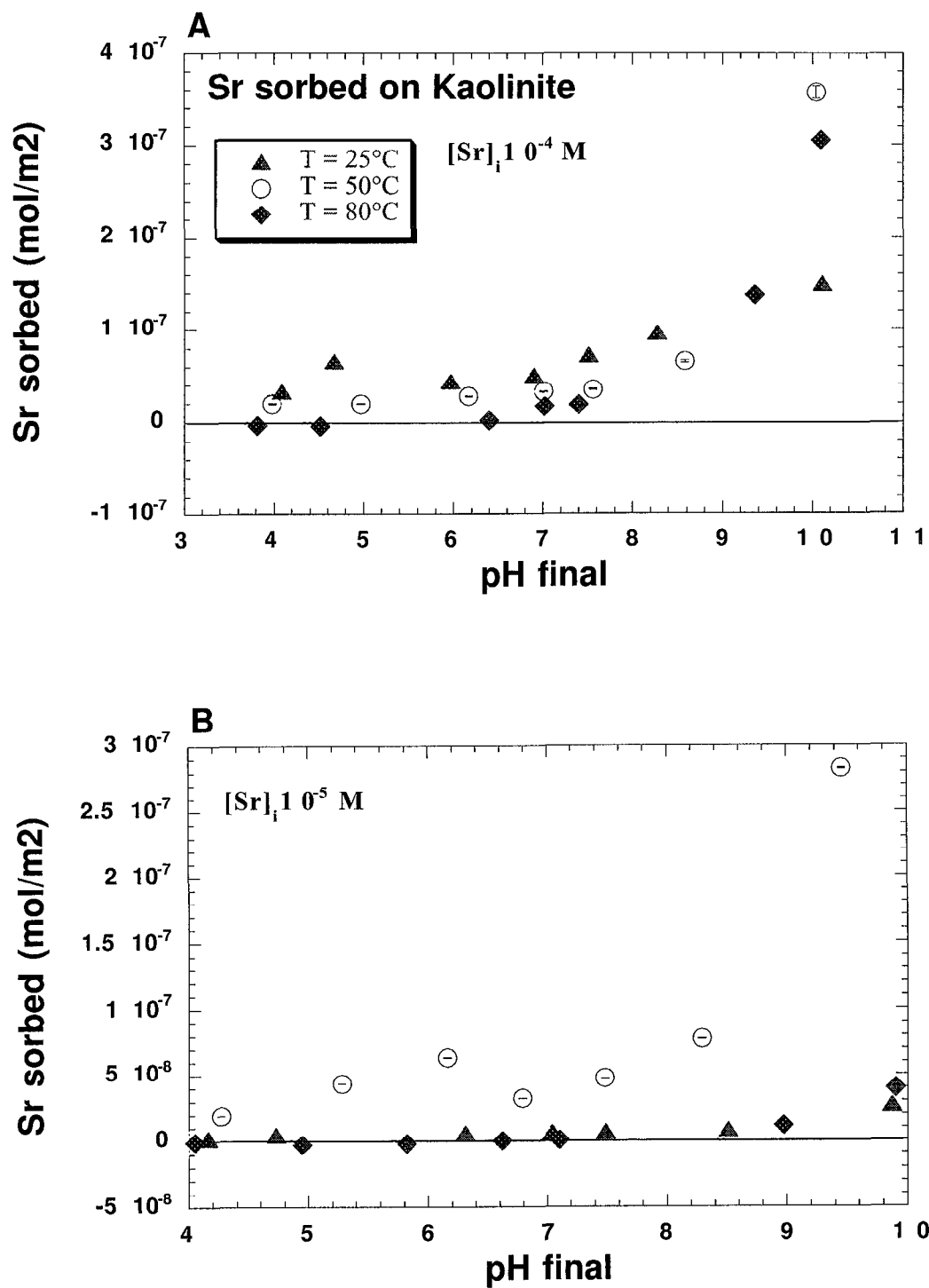


Figure 3. Strontium-uptake at kaolinite surface as a function of pH at 25, 50

and 80°C from solutions containing initial Sr concentrations **A** $[\text{Sr}]_i = 10^{-4} \text{ M}$, **B** $[\text{Sr}]_i = 10^{-5} \text{ M}$, **C** $[\text{Sr}]_i = 10^{-6} \text{ M}$, **D** $[\text{Sr}]_i = 10^{-7} \text{ M}$.

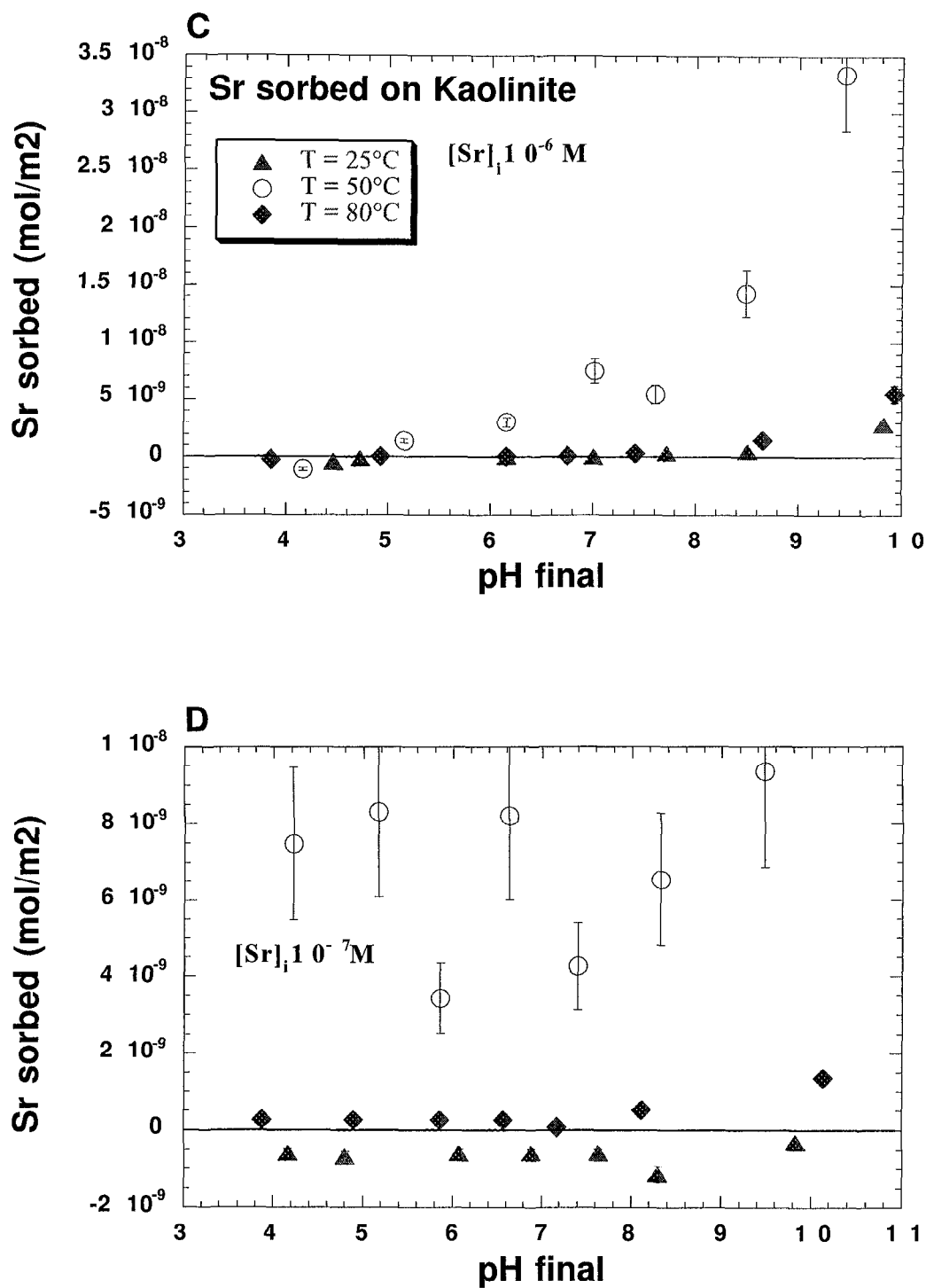


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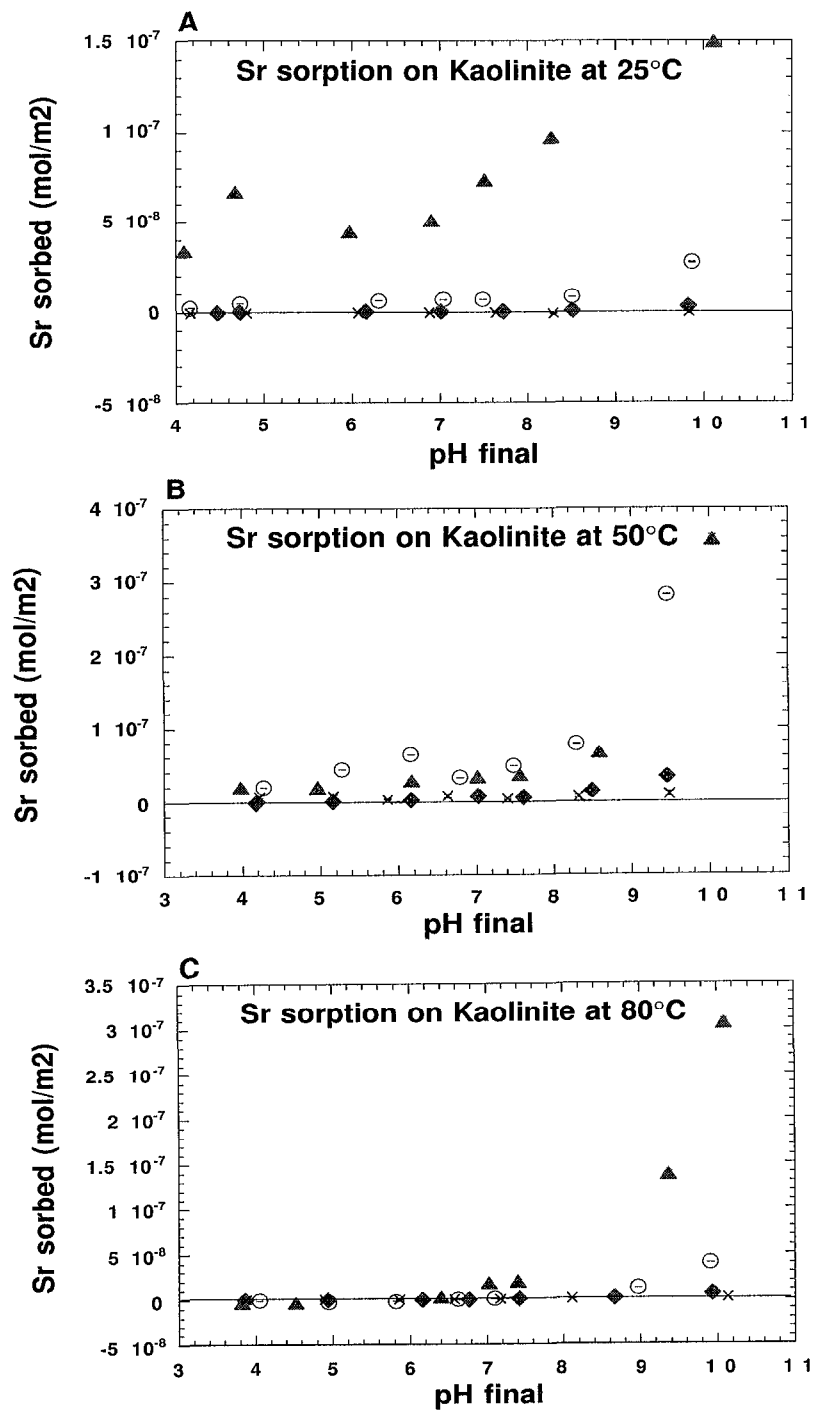


Figure 4. Strontium-uptake at kaolinite surface as a function of pH and initial Sr concentration at **A** 25°C, **B** 50°C, and **C** 80°C.

experiments with $[\text{Sr}]_i = 10^{-6}$, 10^{-5} , and 10^{-4} M. At $[\text{Sr}]_i = 10^{-7}$ M, any temperature dependence of Sr-uptake is masked by analytical uncertainty. The final dissolved Sr concentrations approach or exceed strontianite saturation at pH > 7.

Similar to goethite, significant Sr-uptake occurs at 25, 50, and 80°C from solutions containing pH > 8 and $[\text{Sr}]_i = 10^{-6}$ to 10^{-4} M (Fig. 5 and 6). Minimal Sr is removed from solutions containing $[\text{Sr}]_i = 10^{-7}$ from pH 4 to 10. The absolute Sr-uptake increases with increasing $[\text{Sr}]_i$ at constant temperature and at pH > 8. In contrast to Sr-uptake on goethite, Sr-uptake on kaolinite has a complex dependence on temperature. At $[\text{Sr}]_i$ of 10^{-4} M, there is no temperature dependence for Sr-uptake. However at $[\text{Sr}]_i = 10^{-7}$ to 10^{-5} M, Sr-uptake is higher at 50°C than at 25 and 80°C.

2. Spectroscopy

We are currently optimizing sample preparation for x-ray absorption spectroscopy to determine the molecular structure of Sr-uptake. Preliminary results show first shell of about 8-9 oxygen atoms at about 2.6 Å around the central Sr atom. From this data we cannot distinguish between Sr sorption to OH or CO₃ surface sites. Nor can we distinguish between mono- and multinuclear sorption, because low signal-to-noise ratio was too low to obtain useful information beyond the first shell. Future samples will have greater surface loading and be run for longer scan times to acquire second shell information. Part of the problem in obtaining structural information for Sr beyond the first shell by XAS is the possibility that Sr²⁺ remains relatively hydrated when it adsorbs. If this is the case, it would be useful to apply other, complementary spectroscopic tools such as Infra-Red (IR), Raman and Nuclear Magnetic Resonance (NMR), to the problem of determining the nature and structure of the Sr - surface species.

We have already begun to investigate these other possibilities. We have obtained some preliminary NMR spectra for kaolinite, using ²⁷Al and ²⁹Si. The early results indicate that ²⁹Si NMR might be a promising tool for kaolinite and montmorillonite. Goethite cannot be run because Fe³⁺ is paramagnetic. The ²⁷Al NMR spectra showed a homogeneous octahedral environment for both the "clean" kaolinite and the Sr - sorbed kaolinite. The ²⁹Si NMR, however, shows the possible formation of an amorphous silicate layer at the surface of the Sr - sorbed kaolinite, which is absent in the case of the "clean" kaolinite.

If indeed, Sr remains relatively hydrated at the surface, then IR vibrational frequencies should be observed at about 3597-3496 cm⁻¹, where the -OH stretching frequency for Sr(OH)₂ is located. Unfortunately, this is also the frequency range where bulk water has a broad -OH stretching peak, and can mask the Sr-OH peak. We are currently in the process of developing an experimental protocol for eliminating the problem with the bulk H₂O peak.

3. Review of thermodynamic and sorption data bases

Our initial thermodynamic data bases are the mineral and aqueous GEMBOCHS data base (version data0.com.V8.R6; Johnson and Lundeen, 1997) and the surface complexation data base (Dzombak and Morel, 1990) associated with the Geochemist's Workbench applications package (Bethke, 1996). The GEMBOCHS data base is maintained to support the EQ3/6 geochemical modeling code package (Wolery, 1992; Wolery and Daveler, 1992) and has been specially formatted to work with The Geochemist's Workbench applications. We have added internally consistent Sr-carbonate data from Busenberg et al. (1984). There is a lack thermodynamic data for goethite at elevated temperature as a function of particle size; Fe^{3+} -carbonate aqueous species; and Fe^{3+} -hydroxide and SrNO_3^+ aqueous complexes as a function of temperature.

There are several short-comings to Dzombak and Morel (1990) surface complexation data base describing Sr-uptake to hydrous ferric oxides, such as goethite. They fit experimental data from Kolarik (1961) to obtain intrinsic surface complexation constants for Sr sorption to hydroxyl sites only, assuming a generalized two-layer surface complexation model, no aqueous Sr-nitrate or Sr-carbonate complexes, and no surface Sr-carbonate complexes or precipitates. In this system both aqueous and surface carbonate complexes are very important. Carbonate surface complexes form on hydrous iron oxides (Van Geen et al., 1994; Zachara et al., 1987). Additionally, Na and NO_3 in background electrolytes solutions are assumed to be non-sorbing. However, Rundberg et al., (1994) report Na sorption onto goethite at 25°C in NaClO_4 mediums with ionic strengths of 0.005 to 0.016. No NO_3 sorption data is available.

Summary of Accomplishments

There are two major conclusions from these preliminary Sr sorption experiments:

- Strontium-uptake may occur at metal-oxygen or metal-carbonate surface sites, or as a Sr-carbonate surface precipitate;
- Changes in temperature may not effect Sr-uptake.

The data survey reveal that the following should be acquired, estimated, or further evaluated:

- thermodynamic data for Fe^{3+} -hydroxide aqueous complexes at elevated temperature
- thermodynamic data for Fe^{3+} -carbonate aqueous species
- thermodynamic data for SrNO_3^+ as a function of temperature
- thermodynamic data for goethite at elevated temperature as a function of particle size

- surface complexation constants for Sr, Na, CO₃ and NO₃ as a function of temperature

Future research will be directed toward spectroscopic analysis of reaction run products to determine the molecular structure of Sr at goethite and kaolinite surfaces. It is not necessary to determine the molecular structure above 25°C, because macroscopic batch experiments do not indicate a change in reaction mechanism. Future sorption experiments will determine the rate of Sr-uptake to kaolinite and goethite in flow-through reactors from conditions undersaturated to supersaturated with respect to strontianite at 25, 50, 80°C. The advantage of flow-through reactors over batch reactors is the solution composition can be held constant over the duration of the experiment. This allows the effect of saturation on the overall uptake rate to be investigated. These experiments will be followed by long-term desorption experiments. Batch sorption experiments will be conducted as needed to support the kinetic experiments and spectroscopic analysis.

Papers and Abstracts

None during the first year of research.

REFERENCES

- Bethke, C.M. (1996) *Geochemical Reaction Modeling*. Oxford Univ. Press, New York, 397 pp.
- Busenberg, E., Plummer, L.N. and Parker, V.B. (1984) "The solubility of strontianite (SrCO₃) in CO₂-H₂O solutions between 2 and 91°C, the association constants of SrHCO₃⁺(aq) and SrCO₃⁰(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr²⁺(aq) and SrCO₃(cr) at 25°C and 1 atm total pressure." Geochim. et Cosmochim. Acta, 48: 2021-2035.
- Duncan, P. R. (1995). An evaluation of the potential for remediating hazardous metals and radionuclides in aquifers and the subsurface: A summary report., INEL, Biotechnology Group.
- Dzombak, D.A. and Morel, F.M.M. (1990) *Surface Complexation Modeling: Hydrous Ferric Oxide*: John Wiley, New York, 393 pp.
- Johnson, J.W. and Lundeen, S. R. (1997) "GEMBOCHS thermodynamic datafiles for use with the EQ3/6 software package" Lawrence Livermore National Laboratory UCRL-ID, in prep.
- Kolarik, Z. (1961) "Sorption radioaktiver Isotopen an niederschlagen. VI. System Eisen(III)-Hydroxyd-Strontiumnitratlösung und die allgemein gesetzmässigkeiten der sorption am Eisen(III)-Hydroxyd." Collection Szech Chem. Commun 27: 929-933.

- Newmark R.L. and Aines R.D. (1995) Summary of the LLNL gasoline spill demonstration- Dynamic underground stripping project: Lawrence Livermore National Laboratory UCRL-ID-120416, 36 p.
- O'Day, P. A., Brown, G. E. Jr., Parks, G. A. (1994). "X-ray absorption spectroscopy of cobalt(II) multinuclear surface complexes and surface precipitates on kaolinite." J. Colloid Interface Sci. **165**: 269-289.
- Rundberg, R.S., Albinsson, Y. and Vannerberg, K. (1994) "Sodium adsorption onto goethite as a function of pH and ionic strength." Radiochim. Acta **66/67**: 333-339.
- Scheidegger, A. M., Lamble, G. M., Sparks, D. L. (1996). "Investigation of Ni sorption on pyrophyllite: An XAFS study." Environ. Sci. Technol. **30**: 548-554. Schindler, P.W., 1967, Heterogeneous equilibria involving oxides, hydroxides, carbonates, and hydroxide carbonates. In *Equilibrium Concepts in Natural Water Systems*, (W. Stumm, ed.): Advances in Chemistry Series 67, Am. Chem Soc., p. 196.
- Sillen, L.G. and Martell, A.E. (1964) *Stability constants of metal-ion complexes: Chem. Soc. Spec. Pub. 17*, London.
- van Geen, A., Robertson A. P., Leckie J. O. (1994). "Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters." Geochim. Cosmochim. Acta **58**: 2073-2086.
- Wolery T.J. (1992) "EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide, and related documentation (Version 7.0)" Lawrence Livermore National Laboratory UCRL-MA-110662 PT III.
- Wolery T.J. and Daveler S.A. (1992) "EQ6, a computer program for reaction path modeling of aqueous geochemical systems: Theoretical manual, user's guide, and related documentation (Version 7.0)." Lawrence Livermore National Laboratory UCRL-MA-110662 PT IV.
- Zachara, J.M., Girvin, D.C., Schmidt, R.L. and Resch, C.T. (1987) "Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions." Environ. Sci. Tech. **21**: 589-594.

**Hydrologic and Geochemical Controls on the Transport of
Radionuclides in Natural Undisturbed Arid Environments
as Determined by Accelerator Mass Spectrometry**

Earth and Environmental Science Directorate
Lawrence Livermore National Laboratory
October 1997

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Research Objectives

This research develops techniques for measuring globally distributed ("fallout") radionuclides occurring in extremely low abundances, and then applies these techniques to address radionuclide migration in arid unsaturated soils. Migration through these soils is of central importance to the assessment of public health risk from contaminant releases and the assessment of the safety of nuclear waste storage facilities. The techniques employ accelerator mass spectrometry (AMS), a relatively new analytical tool that permits this work to be conducted for the first time. The radionuclides of interest were globally distributed by the atmospheric nuclear weapons test fallout of the 1950'-1960's - and therefore are today present in all microenvironments, though in very low concentrations. Because these nuclides originated from thermonuclear events, they are generally the nuclides of most concern when assessing the extent of and risk from actual or potential radioactive contamination. The ability to measure these nuclides in low concentrations in any environment has several advantages. First, the AMS techniques will permit us to focus radionuclide migration investigations and research on the zones surrounding the contamination zone itself. Most sites contaminated with radioactivity are also altered in other ways - for example, they may be contaminated by VOC's, or the sites have been significantly disrupted by construction activities and land movement (bulldozing, trenching, etc.). It is impossible to understand how the nuclides will behave once they migrate beyond the area of alteration by only examining their behavior within the altered area. Second, the AMS techniques will permit us to avoid having to conduct radionuclide migration research in highly contaminated areas. Field studies of migration commonly must be conducted in highly contaminated areas, simply because that's where the nuclides occur in concentrations that are large enough to measure by existing techniques. There are drawbacks in doing this: the samples themselves are radioactive waste, which are difficult to deal with in the field and laboratory, and they must later be expensively disposed of as mixed waste. Third, the AMS techniques will allow radionuclide migration studies to be conducted within the "far-field" environment, the environment of the receptor human populations. This information is the basis for risk assessment analyses of the actual threat from radioactive contaminant releases, or of the potential future risk from nuclear waste storage facilities. The fallout nuclides occur in these environments today, but in concentrations that require AMS techniques. These three advantages will result in more reliable site investigations and radionuclide migration research at far less expense. We have chosen to focus our initial work on unsaturated soils because it allows us to build upon previous research, because most of the contamination in the United States is within unsaturated soils, and because this environment is the primary interest for long-term storage of nuclear waste.

Research Statement

There are four research components: (1) developing AMS techniques for ^{90}Sr - ^{93}Zr - ^{99}Tc - ^{129}I analysis; (2) improving AMS ^{36}Cl and chlorine methods for determining

moisture flux in arid soils; (3) measuring the distribution of ^{90}Sr - ^{93}Zr - ^{99}Tc - ^{129}I relative to the moisture flux in an unsaturated zone soil as defined by chloride and ^{36}Cl movement; and (4) developing a numerical model simulating the migration which produced the observed distribution.

Component 1. Table 1 provides information about the nuclides targeted by this project for analytical development by AMS techniques. For each of the nuclides, the current estimated abundance in soils due to global fallout (the measured ratio, or the atoms/g for ^{99}Tc) is several orders of magnitude too low for accurate and rapid measurement by techniques other than AMS. Our previous work has demonstrated that AMS has the capability to measure abundances for each of these nuclides at levels several orders of magnitude lower than the estimated fallout amounts given in Table 1. Although not specifically targeted for this project, other radionuclides, such as ^{53}Mn , $^{59}\text{-or-}^{63}\text{Ni}$, and ^{79}Se , have potential for development by AMS. We begin, however, with ^{90}Sr , ^{93}Zr , ^{99}Tc , and ^{129}I because: 1) we feel confident the analytical techniques can be developed, 2) the nuclides are important for health risk assessments, and 3) they can serve as analogues to other classes of nuclides that are also important contaminant species.

Table 1. Nuclides Targeted for AMS Development Under the EM Science Program						
Radio-nuclide	Activity/ μg (pCi)	Fission Mass Yield	Measured Ratio	Natural Amounts in Soils	Thermonuclear Global Fallout in Soils in 1998	Value to ER/EM Objectives
^{129}I	1.73E+02	0.74%	$^{129}\text{I}/^{127}\text{I}$	1.20E-12 ($^{129}\text{I}/^{127}\text{I}$)	1.0E-09 ($^{129}\text{I}/^{127}\text{I}$)	Used to determine mobility of anionic species in soils. Tracing of ^{129}I contamination at DOE sites (e.g., Hanford). Used to determine moisture flux in unsaturated soils (needed for nuclear waste facility licensing).
^{90}Sr	1.37E+08	5.91%	$^{90}\text{Sr}/\text{Sr}$	1.00E-21 ($^{90}\text{Sr}/\text{Sr}$)	1.0E-11 ($^{90}\text{Sr}/\text{Sr}$)	Used to determine mobility of reactive cationic species through soils. Tracing of ^{90}Sr contamination at DOE sites (e.g., NTS). Used to assess public health risks from contaminant migration.
^{99}Tc	1.70E+04	6.10%	^{99}Tc atoms	<1.0E+04 atoms/g	>1.0E+09 atoms/g	Used to determine mobility of anionic species in soils. Tracing of ^{99}Tc contamination at DOE sites (e.g., NTS). Used as an early indicator of nuclear contaminant migration.
^{93}Zr	2.56E+03	6.38%	$^{93}\text{Zr}/\text{Zr}$	1.00E-13 ($^{93}\text{Zr}/\text{Zr}$)	5.0E-09 ($^{93}\text{Zr}/\text{Zr}$)	Used to determine mobility of non-reactive cationic species through soils. Used to determine mobility of nuclear reprocessing wastes.
^{36}Cl	3.30E+04	---	$^{36}\text{Cl}/\text{Cl}$	<1.00E-12 ($^{36}\text{Cl}/\text{Cl}$)	>1.00E-12 ($^{36}\text{Cl}/\text{Cl}$)	Used to determine mobility of anionic species in soils. Used to determine moisture flux in unsaturated soils (needed for nuclear waste facility licensing). Presence of ^{36}Cl in deep soils or ground water can indicate rapid transport of water.

Component 2. While the analytical techniques for ^{36}Cl are already well developed, there are other aspects of its use in radionuclide migration studies that must be

examined as part of this study. Among the targeted radionuclides ^{36}Cl is unique because it is useful in revealing the extent and rate of moisture flux within the soil. Chloride is believed to move conservatively with soil water, and the distribution of ^{36}Cl indicates the extent of and pathways for moisture movement since the early 1960's, the height of ^{36}Cl fallout. However, there are several aspects to the reliable and robust usage of chlorine and ^{36}Cl that still require development. Therefore, an important part of this research on radionuclide migration is to make ^{36}Cl a more reliable indicator of moisture flux by a numerical characterization of the relationship(s) between ^{36}Cl migration, stable chloride flux, soil physical parameters, and moisture flux.

Component 3. As a demonstration of the developed AMS analytical techniques, and as a useful application characterizing their migration in unsaturated soils, the concentrations of the fallout radionuclides will be measured from unsaturated soils in the desert southwestern United States. As a study of their migration parameters, the measurements will be made in conjunction with our study of the use of ^{36}Cl to characterize moisture movement (Component 2). A trench in excess of 5 meters will be excavated and soil samples will be collected from the trench wall. This will permit: 1) a good distribution of sampling, 2) the determination of sample location relative to geological features of the soil, and 3) the collection of soil physics data required for numerical modelling.

Component 4. In order that our results characterizing radionuclide migration at the trench site be capable of more universal application, a numerical model will be developed using the LLNL NUFT (Non-isothermal Unsaturated Flow and Transport) computer code. The model will simulate the observed migration at the site. The NUFT model is a three-dimensional, finite-difference discretization code that permits parameter input of soil temperature variation with time, solute dispersion and diffusion, as well as the governing soil physics characteristics.

Research Progress

Development of AMS ^{129}I Techniques. A significant amount of work during FY97 went into the AMS instrumental analytical procedures needed to measure ^{129}I . Sufficient improvements were made on sputtering efficiency, maximizing beam current, detection efficiency, and elimination of isobaric interferences that we now feel reliable ^{129}I analyses can be made at a background level of $^{129}\text{I}/\text{I} \approx 10^{-13}$. This is more than adequate to measure natural ambient $^{129}\text{I}/\text{I}$ levels in arid soils, and certainly adequate to measure anthropogenic (bomb-pulse or contaminant) levels. To demonstrate this, we performed two experiments. First, we measured ^{129}I concentrations in a soil with "known" ^{129}I concentrations. Measurement of ^{129}I at levels comparable to those achievable with AMS is so rare that it was difficult to locate "standard" samples to demonstrate our techniques. One sample that is available contains ^{129}I concentrations that overlap the levels measured by neutron activation and AMS. It is a soil collected in the vicinity of

Chernobyl and distributed by the IAEA, denoted IAEA-375. Neutron activation techniques have determined the ^{129}I concentration to be 1.2×10^9 atoms/gram (20% uncertainty). Figure 1 shows the results of our AMS determination of the ^{129}I concentration of this soil obtained in the last year.

Within analytical uncertainties there is good agreement between our AMS measurements and those determined by neutron activation. These results demonstrate both the reliability of the AMS measurement itself and the chemical extraction method employed to release the ^{129}I from the soil. For this set of experiments a distillation technique in which the sample was boiled in HNO_3 and H_2SO_4 was utilized. The ^{129}I concentrations obtained for this soil were reproducible independent of both the chemical form of the added stable iodine carrier and chemical yield. These clearly indicate complete isotopic mixing of the carrier iodine and the ^{129}I indigenous to the sample.

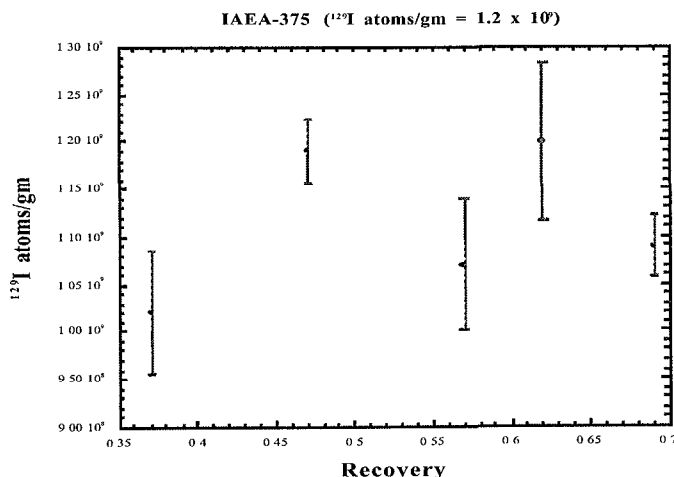


Figure 1

Iodine-129 ratio of IAEA-375 soil sample as determined at LLNL by AMS. Abscissa indicates the fractional yield of iodine in the five separate sample aliquots. All analyses agree with the IAEA accepted value (1.2×10^9) within twenty percent.

The second set of experiments to determine the adequacy of our methods to measure natural levels of ^{129}I involved “garden variety” soil samples. Figures 2 shows the results of ^{129}I measurements on a soil sample collected in the vicinity of Livermore, California.

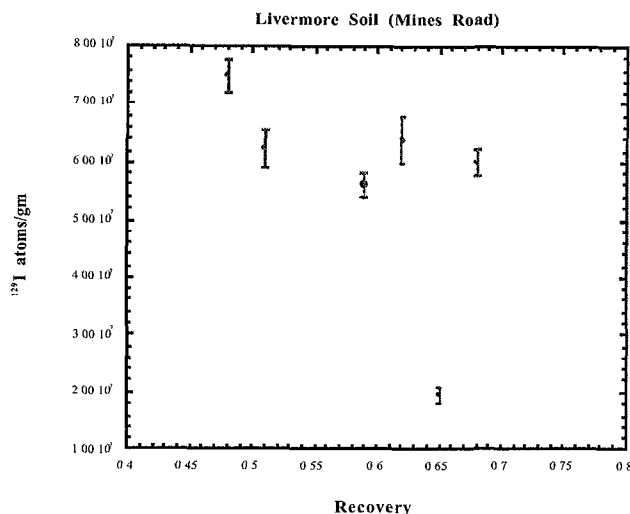


Figure 2

Iodine-129 in a natural soil sample from Livermore, California area. Abscissa indicates the fractional yield of iodine in the six separate sample aliquots. No accepted value for ^{129}I concentration is known for this sample, but close agreement in analyses at about 6×10^7 suggests this value. No attempt to homogenize sample aliquots was made, thus the single low value may represent sample diversity rather than an incorrect analysis.

This soil serves as a proxy for the soils collected at the NTS. With the exception of one anomalous result, these analyses indicate that reliable ^{129}I results can be obtained on natural samples. It is worth noting that for this soil sample no particular attempt was made to homogenize the various constituents. It is not unreasonable that some variability among aliquots occurs. Thus we believe each of the analyses is a reliable indication of the ^{129}I concentration in that sample.

Although the purely instrumental or machine-analytical aspects of this study are both time consuming and of central concern to the project goals, a second major component of this work is the identification of the processes influencing the mobility of ^{129}I in the vadose zone. Factors such as the binding of iodine to clays or organic material probably play an essential role in its mobility. No matter how reliable our mass spectrometry techniques are, valuable results depend on being able to analyze the appropriate samples in the appropriate manner. We are developing two complimentary techniques to identify the factors influencing iodine mobility in the vadose zone: sequential leaching of iodine from soils and physical separation of potentially significant components within soils.

Initial tests of a sequential leaching technique indicate that not all of the iodine in arid soils occurs in the same chemical setting. Conceptually, the iodine resident in soils is either leachable (residing in pore waters or loosely adsorbed on the grain surfaces), fixed (strongly sorbed on clays or in humus or plant tissues), or insoluble. Different soils may be expected to have different proportions of these various constituents. Our initial results on the proxy soil from Livermore indicate that $< 20\%$ is leachable in

water. This result is somewhat surprising since iodine is regarded as a “conservative” species that readily migrates with water. Further tests indicate that smaller proportions are leachable in basic or mild acid solutions. Although these are only initial results, it may be the case that considerable ^{129}I in this particular soil resides on clays or in organic matter. Further tests in the near future are designed to address this question and should clarify the siting of ^{129}I in these samples.

Physical separation of samples for ^{129}I analysis is not as trivial as sieving or optical separation, followed by AMS analysis. Any significant processing or handling of samples can cause mechanical separation of ^{129}I from its in-situ locality. From this perspective, the sequential leaching experiments, conducted on samples with minimal handling, were easier to conduct and the most appropriate starting point. The determination of the extent to which physical handling of ^{129}I samples can bias scientific results is a goal of the work planned for FY98. Our intent is to compare results from samples with this type of physical handling to samples with only sequential leaching processing. The benefit of developing physical separation techniques is that ^{129}I siting can be better examined because the phases can be isolated, and the precise site locations can be known with greater confidence.

In summary, we have demonstrated our capability to reliably analyze environmental levels of ^{129}I . The challenges of understanding the natural behavior of this geochemically complex element, and how this affects the distribution of anthropogenic ^{129}I in arid soils, lie ahead. This will be the focus of work during FY98.

Development of AMS ^{99}Tc Techniques. During early FY97 we performed preliminary tests which demonstrated the technical feasibility of AMS for the detection of ^{99}Tc . This feasibility work has been followed during the remainder of FY97 by more extensive development work on the AMS and ion detection parameters, detection sensitivity, and methods for the extraction of ^{99}Tc from soils.

The lack of a stable technetium isotope presents a number of technical challenges for AMS measurements which are not present for other AMS isotopes, such as ^{129}I , in which the stable isotopes serve multiple roles as yield monitor, chemical carrier, and sample matrix. Measurements of radioactive-to-stable isotope ratios (e.g., $^{129}\text{I}/^{127}\text{I}$) are then implicitly corrected for time- and sample-dependent variations in a number of factors such as chemical recovery, ionization efficiency, acceleration efficiency, and ion transport through the spectrometer. To allow AMS measurement of ^{99}Tc , some other element (or collection of elements) must be used as a sort of proxy, to fill these same roles. The requirements of this proxy are: a stable isotope near, but not at mass 99; reasonable negative ion production; good thermal and electrical conductivity; and a chemistry as near as possible to that of Tc. We have explored two candidates for this, silver and rhodium, both of which have positive and negative features.

By far the largest uncertainty going into this project was whether it would be possible to get reproducible ratios between isotopes of different elements when there are several factors in chemistry, negative ion production, and ion acceleration that could lead to large degree of fractionation between isotopes of the different elements. A further challenge is presented by interference from Ruthenium-99, a stable isobar of

^{99}Tc . This interference cannot be removed using the spectrometer, and must be chemically separated from the technetium in the sample and from the matrix material. An advantage of AMS in this respect is the high energy to which the ions are accelerated, which allows the use of nuclear physics particle detection techniques for post-spectrometer particle identification (Figure 3).

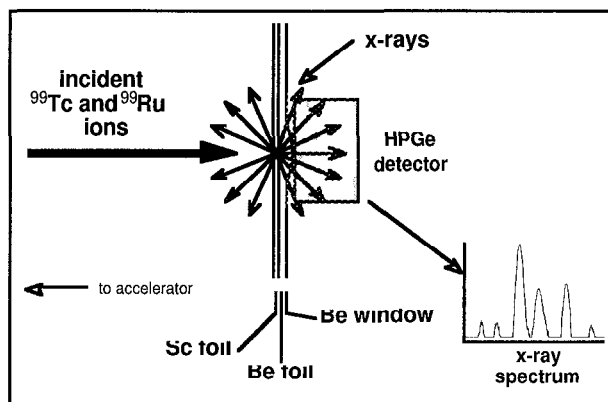


Figure 3

Detection of ^{99}Tc ions using characteristic projectile x rays. Following analysis in the AMS spectrometer, the ions are incident on a target foil. The induced x rays are detected with a HPGe detector. A Be absorber is included to stop the ions and to attenuate low energy x rays.

This enables additional rejection of certain interferences, including atomic isobars, easing the requirements for the chemical separation and reducing the ambiguity present in identifying ions by mass only.

During FY97, preliminary tests were performed to address the following questions: 1) the behavior of technetium and rhodium in the ion source, including the intensity and efficiency of the negative ion production; 2) the charge states and energies accessible for mass 99 using the LLNL AMS spectrometer; 3) the detection efficiency for mass 99 ions and the rejection of Ru-99 using characteristic projectile x-rays; 4) the potential existence of unanticipated interferences; and 5) the reproducibility of measured $^{99}\text{Tc}/^{103}\text{Rh}$ ratios.

The results of these tests showed acceptable ^{99}Tc negative ion currents from the cesium sputter source, high detection efficiencies using characteristic projectile x-rays, and reasonable $^{99}\text{Tc}/^{103}\text{Rh}$ ratios which were reproducible at the 10-15% level over time and for standards varying by over an order in ratio (Figure 4).

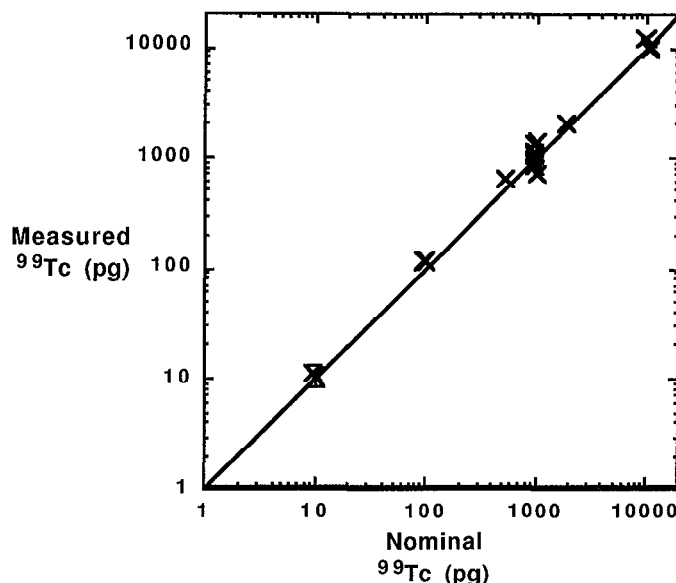


Figure 4

Measurement of ^{99}Tc in standards by AMS using rhodium carrier.

We believe this work was the first demonstration of significant Tc current from a cesium sputter source. Overall detection efficiencies sufficient to allow the detection of ~ 10 fg of ^{99}Tc in 10-15 minutes were observed. In addition, we found that the present AMS facilities at LLNL were sufficient to accelerate, transport, and analyze mass-99 ions at useful energies and charge states. Finally, no unanticipated interferences were observed at the level of sensitivity of the preliminary tests.

Two significant problems were uncovered during the development work — unacceptably high ruthenium levels in the ultra-pure rhodium stock material, and the presence of an interference from sulfur which could not be removed using the characteristic x-ray detector. The natural abundance of ruthenium in the environment is quite low, and most materials should not have a sufficiently large ruthenium content to represent a problem in our measurements. However, an exception to this is rhodium, which is typically found in connection with ruthenium in nature. The rhodium stock material that we purchased for our work, which is ultra-pure by normal standards, had several orders of magnitude more ruthenium than was acceptable.

To reduce the level of ruthenium in the rhodium stock solution, we developed a chemical purification procedure which involves oxidizing the ruthenium to the volatile species ruthenium tetroxide, then removing it by vacuum distillation. The process is simple and effective, reducing the ruthenium to within a factor of 10 of the required level, which is ~ 10 ppb Ru/Rh. A number of options are available that we can try either to further reduce the ruthenium level, or to reduce the amount of rhodium carrier which is required.

A second unanticipated problem was the discovery of an interference from sulfur, which has an x-ray line which overlaps with the technetium x-rays. The preliminary tests indicated that this interference could be eliminated by the proper choice of ion

charge state and accelerator parameters. In addition, the production of these x-rays is very much suppressed relative to the technetium x-rays. However, with the experience and improved sensitivity which was gained during the development work, it became clear that this interference would not continue to be a problem.

To address the sulfur interference, we are now using a hybrid detection system, in which a thin gas ionization detector is placed in front of the characteristic x-ray detector. This system very cleanly discriminates against sulfur and other interferences which are well separated from Tc in the periodic table. The next most favorable alternative to rhodium as a carrier is silver. Silver has several advantages over rhodium — it is significantly less expensive, is more readily available, and is inherently orders of magnitude cleaner of ruthenium. The major disadvantage is that silver is much farther from ^{99}Tc in both atomic number and mass, increasing the possibility for widely varying measured ratios. In addition, we avoided silver during the early development work because the silver isotopes produce overwhelming interferences at the charge states which minimized the sulfur interference.

A byproduct of the hybrid detection system is that, because it so cleanly discriminates against sulfur and other interferences, it has allowed us to explore charge states in which silver is not an interference. In our first tests with silver, we have demonstrated reproducible ratios for standards (Figure 5), and have shown that stock silver from the chemical supplier is cleaner of ruthenium than our processed rhodium, and appears to be sufficient for use as is.

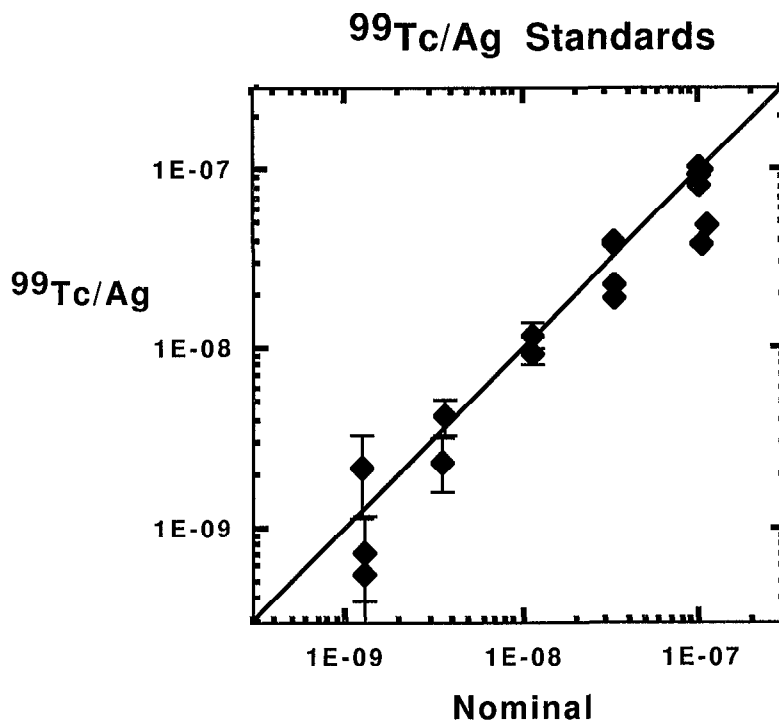


Figure 5

Measurement of ^{99}Tc in standards by AMS using silver carrier. The observed deviations for the highest standards were caused by a drift

in the accelerator conditions. The deviations for different standards were consistent, and the overall deviation was removed with correction of the accelerator conditions.

In summary, we have demonstrated sub-picogram detection sensitivity for ^{99}Tc using both rhodium and silver carriers. We are currently optimizing the methods using silver carrier and the hybrid detection system, and expect to reach the necessary sensitivity using this combination in early FY98. We have also been working for the past few months on methods for the extraction of ^{99}Tc from spiked soil samples, using up to a few hundred grams of soil. Chemical recovery is so far somewhat low (~60% soil-to-measured-sample), but still sufficient for AMS analytical work and seemingly reproducible at this level. The lack of soils with known concentrations of ^{99}Tc (i.e., “standard” soils) hampers this work, but is an unavoidable problem when developing state-of-the-art analytical techniques.

Excavation of a Deep Trench for Soil Sampling. We chose to trench on the Nevada Test Site because we believed some of the logistical problems of this moderate-scale construction project could be more easily overcome at this well-used site. Still, NEPA documentation, archeological clearances, OSHA regulations, cost estimations, site “ownership” questions, and simple manpower deficiencies delayed excavation for several months during FY97. The trench was finally completed in September, the trench wall was mapped for geological structure, stratigraphy, and soil composition, and more than 150 soil samples were collected. Additionally, approximately 30 rock samples (cobbles) were collected from the trench wall for the purpose of exposure-age dating that could help to better define the depositional history of the trench sediments. The trench was located in Area 2 of the NTS, adjacent to the Carpetbag geological fault. Trench dimensions are approximately 5 meters deep, 14 meters long at this depth, and 12 meters wide. It required approximately two days with a bulldozer and grader to excavate the trench. The south trench wall was benched at approximately 5 foot intervals for OSHA safety, and this permitted ease of sampling. The north trench wall was sloped to prevent collapse and was not sampled. Each end of the trench was ramped to allow easier access. The trench will remain open for several months to allow the further sampling planned in this study, and is available for any other scientific use that will not interfere with this sampling. We have contacted DOE-NV (Las Vegas) inquiring about any interest they would have in using this trench, or in collaborative work.

Samples were collected in six vertical transects from land surface to the bottom of the trench. Samples were taken every 25 cm, which allowed both thorough spatial coverage and a complete sampling of all levels of soil stratigraphy. All soil units were sampled by this strategy. Two of the transects were “baseline” transects that intersected no structural features of the soil. The other four transects sampled obvious fractures in the soil, one containing abundant carbonate infill, one containing, moderate carbonate, one free of carbonate, and the final transect along the “contact” of the carpetbag fault vein infilling and the non-carbonate soil external to the fault zone

proper. If there are preferential pathways to moisture and radionuclide migration, it is believed they would be along sites such as these.

Summary of Accomplishments

- Data have been collected from several test soils that have ^{129}I concentrations ($^{129}\text{I}/\text{I}$ ratios) sufficiently high that AMS techniques overlap with other, less sensitive techniques. All of the AMS values agree well with those from the other techniques, with twenty percent agreement between AMS values and neutron activation values for test sample IAEA-375. The accuracy is achieved regardless of absolute chemical yield obtained by our sample processing methods. This result is excellent in consideration of the complexity of the sample processing methods, and the natural heterogeneity within the test soils.

- Results from sequential leaching experiments indicate that <20% of the ^{129}I in a soil from a semi-arid region is water leachable (i.e., presumably water soluble). This is an important result both from the standpoint of sample processing intended to remove iodine, and because of its potential implications for ^{129}I and stable iodine migration.

- Tests on AMS spectrometer performance with respect to technetium indicate that ^{99}Tc has a sputtering efficiency with a cesium sputter beam sufficient for AMS analysis, that ^{103}Rh can be used as a proxy for a stable technetium isotope ($^{99}\text{Tc}/^{103}\text{Rh}$ ratios were reproducible 10-15% on prepared standards varying by over an order of magnitude), and that detection efficiency using characteristic projectile x-rays was sufficient to permit the detection of ~10 fg of ^{99}Tc in a 10-15 minute analysis.

- Although this year we have developed a technique for effectively removing ruthenium from the rhodium solution we add as a tracer and stable isotope proxy, we have discovered that silver can be used as a proxy in place of rhodium, eliminating the need for rhodium altogether. This was made possible by development of a hybrid detection system that eliminates a variety of interferences associated with stock silver solutions. Our success with both the Rh and Ag techniques permits us to continue exploring the robustness and reliability of both methods simultaneously.

- We have excavated, geologically characterized, and taken a large suite of samples from a trench in alluvial soils on the Nevada Test Site. The trench is slightly over 5 meters in depth and about 16 meters in length. This is the maximum expected depth for the migration of the fallout nuclides to the present time. The samples will be analyzed for soils properties, soil chemistry, and the target radionuclides during FY98.

Papers and Abstracts

McAninch, J.E., Marchetti, A.A., Bergquist, B.A., Stoyer, N.J., Proctor, I.D., Nimz, G.J., Caffee, M.W., Finkel, R.C., Moody, K.J., Sideras-Haddad, E., Buchholz, B., and Esser, B.K., 1997. Development of AMS for detection of ^{99}Tc : Preliminary Investigations. Invited talk presented at the International Conference on Methods And Applications of Radioanalytical Chemistry - Marc IV, April, 1997. Paper submitted to the Journal of Radioanalytical and Nuclear Chemistry as part of the conference proceedings.

Characterization of Contaminant Transport by Gravity, Capillarity and Barometric Pumping in Heterogeneous Vadose Regimes

Lawrence Livermore National Laboratory
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Progress Report

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Research Objective

For surface spills and near-surface leaks of solvents or other volatile liquid-phase chemicals, the vadose or unsaturated zone may well become a long-term source of contamination for the underlying water table. When a volatile contaminant exists as free product or in dissolved form in the vadose environment, upward transport of the vapor phase can occur with the contaminant ultimately being vented as a vapor into the atmosphere. This transport occurs naturally and can be enhanced by anisotropy resulting from the flow paths of a fault zone or other heterogeneous regime. Several poorly understood stages in the transport process are involved in going from a volatile, liquid state contaminant to a contaminant vapor vented at the surface. For liquid-phase flows, heterogeneity may or may not enhance the downward transport of contaminants to the water table depending on soil properties and the scale of the surface spill or near-surface leak. Our principal objective in this newly initiated research program is to develop the understanding along with the field and modeling techniques required to characterize the response of the vadose regimes at DOE sites to plumes containing volatile contaminants. These techniques can be useful for evaluating sites where contamination presently exists as well as for providing an objective basis to evaluate the efficacy of proposed clean-up techniques. In the future, they might also be used in an environmentally sound way as part of the site-characterization process for determining suitable locations of new DOE facilities capable of introducing contamination into the water table.

Research Statement

Given the primary objective described above, we have pursued the concept of a vadose-zone observatory (VZO) to provide the field laboratory necessary for carrying out experiments necessary to achieve the goals of this research. Our approach is (1) to carry out plume release experiments at a VZO that allows the acquisition of several different kinds of raw data that (2) are analyzed and evaluated with the aid of highly detailed, diagnostic numerical models. Because the soil properties of a single VZO are unlikely to cover the full range of conditions encountered at DOE facilities, at least two and possibly three VZO's spanning a wide range of hydrologic and geologic properties will be constructed and employed during the period of this contract.

The key feature of a VZO is the variety of plume-tracking techniques that can be used at a single site. Electric resistance tomography (ERT) uses vertical arrays of electrodes across the vadose regime that can track electrical resistance changes in the soil as a plume moves across the zone to the water table. These resistance changes can be used to provide

“snapshots” of the plume during its journey across the unsaturated zone. Monitoring wells can be completed at multiple levels in the vicinity of an infiltration site. Sensors such as electrically conducting gypsum blocks for detecting saturation changes, thermistors for monitoring temperature changes, tensiometers for determining local changes in capillarity and pressure transducers for observing changes in gas-phase pressures provide important information about the state of the gas- and liquid-phase dynamics of the infiltration process. Similarly, access ports at different levels can be used to supply gas-phase samples while lysimeters yield liquid-phase samples. With this type of information, the time-dependent chemical signatures of a plume that has been spiked with an array of dissolved tracers may be correlated with each other as well as with the signatures of the above-mentioned sensors that track the physical changes in the vadose regime.

Field Experiments

To evaluate the physico-chemical evolution of a plume release into the vadose zone we have defined several possible experiments that can be carried out at a VZO.

Measurement of the Downward Progress of a Liquid Phase. Periodic withdrawal of a small sample of ground water from lysimeters placed at different levels in the vadose regime undergoing infiltration will permit the determination of the arrival of the liquid component of the plume when a tracer tending to remain in the liquid state such as KBr is detected. [KBr analyses are routinely performed at LLNL using several methods including high performance liquid chromatography and the ion selective electrode method which is the least expensive analytical method.] We conducted a similar experiment at the NTS using LiBr and tritium as tracers. An array of sampling points measured the vertical and horizontal water spreading of a surface drainage feature. Complimentary to the chemical tracking is the use of electrical resistance tomography (ERT) methods to detect the downward passage of the plume. This method has been found by LLNL to be extremely useful for tracking flow fronts in remediation processes, detecting leaks of fluid from tanks and tracking the percolation of that fluid downward through the vadose zone. The LLNL work uses a cross-borehole approach in tracking plumes which implies the availability of appropriately spaced monitoring wells. Alternatively, small bore, shallow holes can be drilled or augered for electrodes. At present the ERT method is being used exclusively during the development of a new combination lysimeter/tensiometer tool by Boris Fabishenko at the Lawrence Berkeley National Laboratory.

Measurement of History of Dissolved Gases in Contaminant Plume. For volatiles, it is not enough to know only about the passage of a liquid-phase contaminant plume through the vadose zone. This experiment permits us to characterize the response of the vadose regime beyond the process of fracture flow and imbibition and consider how liquid-state volatiles can be partitioned into the vapor state in the mixed-phase regime and then removed. A portable membrane inlet mass spectrometer (MIMS) system can be used for cost-effective analysis of many samples because reasonably large amounts of atmospheric xenon can be used as the single dissolved tracer. (Use of rare isotopes of xenon as tracers generally requires the higher sensitivity of a lab-based system.)

Given their low background levels, and their relatively high solubility in water, isotopes of xenon make excellent tracers. Previous tracer work at LLNL has involved dissolving xenon in water for tracking flow from an injection well. In this proposed experiment, we would tag the water that is drip-irrigated into the ground with saturation levels of one xenon isotope. To estimate the effect of dilution, we would also tag the water with a known concentration of KBr which is not particularly volatile. The periodic withdrawal of samples from the lysimeter array at a site and analysis for KBr and isotopic xenon would allow the mapping of the time-dependent distribution of a volatile component in the vadose regime. The effect of dilution would be taken into account by normalizing the xenon concentration to constant values of KBr. Any remaining deficit of xenon would be interpreted as being a result of the partitioning of the volatile xenon into the gas phase. The lysimeter array data would then provide “snapshots” in time of the spatial distribution of a volatile component as partitioning of that component into the gas phase reduced its concentration in the liquid phase.

Measurements of Gas-Phase Overturn in the Vadose Zone. The surface flux of any gas-phase component is dependent on the history of barometric pressure variations. Barometric effects may well determine the exchange rate of gases between the vadose zone and the atmosphere. Because the gas phase of the mixed-phase regime can be saturated by a volatile contaminant that has partitioned into that phase, the exchange rate of atmospheric gas with vadose zone gas can control the rate at which the removal of liquid-state contaminants can occur.

An estimate of the vadose gas exchange rate can be obtained by injecting a cocktail of gas phase tracers (Xe, Kr, Ne, ^3He & sulfur hexafluoride) different levels in the vadose zone. Subsequent to injection, vadose zone gas can be periodically backdrawn through the

tubes and analyzed for tracer concentration as a function of both location within the mixed phase regime and also as a function of the temporal changes in the surface pressure. Several of these gases tend to strongly partition into the gas phase so that it may be assumed that any decrease in them is a result of upward transport and dilution caused by the gradual exchange between the atmosphere and the vadose regime. In turn, the time dependence of the gas exchange rate as given by the time dependent concentration of cocktail can be compared to the time dependent depletion of dissolved gases mentioned above. The comparison of the volatile depletion rate of the liquid state with the vadose gas exchange rate will greatly aid our fundamental understanding of how the atmosphere couples to the water table through the vadose regime. Such an experiment will help us to understand what are the important details of this coupling. From a practical perspective, it will also give an estimate of the efficiency of self-remediation within the vadose zone by chemical partitioning from the liquid to vapor phase and gas exchange. This estimate of the efficiency of self-remediation can be helpful for determining if the application of remediative schemes is really necessary. If soil venting methods are proposed for remediation, the efficiency of self-remediation obtained from this approach can be used as a baseline for evaluating the effectiveness of the proposed soil venting methods.

Numerical Simulation of Vadose Zone Infiltration

This phase of the research represents a major effort to create a highly detailed and quantitative framework that can be used to relate the different of the physical and chemical state of an infiltration process. All experiments described here will be interpreted using diagnostic models that are based on an LLNL developed 3-D, integrated finite difference, multiphase flow and transport code called NUFT that was developed by John Nitao. For improved accuracy in treating problems where numerical diffusion has the potential to be problematic, the code uses a flux corrected transport scheme (FCT) in treating advective fluxes. Hundreds of such diagnostic models were used in preliminary studies involving the creation of soil-gas fluxes by barometric pumping. Any experiment proposed here can be modeled with the code including those exploring the Henry's law partitioning of contaminant from the liquid to the vapor state in the mixed phase regime.

Research Progress

The main thrust of this study to date has been the planning, design and construction of a Vadose Zone Observatory (VZO) on the Lawrence Livermore site near the corner of Vasco Rd and East Ave. The VZO is a well characterized and highly instrumented location for

studying the interaction of an infiltrating synthetic-contaminant plume with the gas and liquid phases of the vadose regime. During FY '97, sixteen multi-purpose monitoring wells were completed within a 30 m by 50 m area overlying a very heterogeneous vadose zone about 20 m thick that is dominated by low-permeability clay layers with some interspersed silty sand/gravel layers. Such layering is typical at sites where braided stream channeling has occurred and represents the lower permeability category of vadose-zone infiltration regimes that will be considered in this study.

Vadose zone infiltration is accomplished by pumping water containing dissolved tracer gases into a central well (see figure 1, well #SIB-INF-012) having a depth of about 5 m. Surrounding the infiltration well are three monitoring wells (#SEA-INF-001, -002, -003) that permit sampling of the gas phase in the vadose zone at multiple levels down to the water table at about 22 m. When they are not being used in the gas-sampling mode, the gas ports in the wells are used to obtain a running record of the barometric pressure at various depths in the vadose zone. This information will be used to assess the ability of barometric pressure fluctuations to drive atmospheric exchange within the vadose zone. One of the monitoring wells also permits the determination of the degree of moisture saturation and temperature at several levels in this zone. A soon-to-be installed tensiometer/lysimeter array developed in cooperation with Lawrence Berkeley National Laboratory will permit liquid samples to be taken from this same well at different levels. Beyond the perimeter formed by the three vadose zone monitoring wells are four electric resistance tomography (ERT) wells (SIB-INF-008, -009, -010, -011) placed on the four corners of an 8m square centered on the infiltration well mentioned above. Each ERT well contains nineteen electrodes distributed uniformly from the surface to a depth of 28 m (6 m into the saturated zone). Another four ERT wells of identical design have been placed on the corners of an eleven m square centered on the infiltration well and rotated by 90 degrees to the inner four-well square pattern. The inner and outer squares will permit the generated plume to be imaged in a number of different planes that will aid in physically characterizing the state of the synthetic plume as a function of time during its journey to the water table. Infiltration is accomplished by a metered flow of water from a 2500 gallon water tank that is plumbed to the central well. Before the water enters the well, noble tracer gases are dissolved into the flow at a preset rate. The first infiltration experiment is scheduled for late October 1997 following the completion of the observatory.

To provide a diagnostic framework for VZO experiments, a detailed numerical model of the site is being developed using NUFT, the LLNL-developed hydrology code. Soil

samples taken throughout the vadose zone have been analyzed to obtain the hydrologic parameters needed for the vadose zone model. Simulations, which can require several days of computer time, will be run on a standalone, 300 Mhz, dual processor Sun workstation. Its one-gigabyte memory will allow the highly detailed multiphase, hydrologic models to be evaluated.

In another phase of the research, Bryant Hudson released water doped with xenon gas into a water-filled stone quarry in southern California in a joint experiment with a local water district. The fractured vadose regime evidently allowed the water infiltrating the vadose zone from the quarry to move rapidly to the vadose zone without making significant contact with the gas phase of the vadose regime. A significant delay in the arrival of the xenon tracer relative to the arrival of a liquid phase oxygen-isotope tracer would have occurred if the infiltrating liquid and vadose zone gases had mixed during the infiltration process. Using the results of analog laboratory models, the absence of the delay may mean that nearly or totally saturated preferential pathways exist in the unsaturated regime to carry water directly to the water table. This suggests that certain classes of vadose regimes may not be good barriers to the contamination of the saturated zone by infiltrating plumes and the possibility of sparging of the descending plume by vadose zone gases may be minimal to nonexistent in some cases.

Summary of Accomplishments

- * Designed and constructed a highly instrumented Vadose Zone Observatory (VZO) following the selection of an LLNL site as characteristic of the low-permeability end-member of heterogeneous vadose regimes. We can obtain information about the physical and chemical states of a time-dependent infiltration regime with this facility.
- * New combination lysimeter/tensiometer under development by LBNL for installation at the VZO facility.
- * Numerous soil samples from the VZO site have been analyzed for both hydrologic and physical properties and the results are being entered into a numerical model of the vadose regime that is based on the LLNL-developed NUFT computer program.

- * Dissolved xenon gas tracers have indicated that rapid flow across a thick and heterogeneous vadose zone can occur before significant contact with the gas phase of the unsaturated regime takes place. This implies that certain classes of vadose regimes may not be good barriers for preventing contamination of the saturated zone by infiltrating plumes.

Papers and Abstracts

Hudson, G.B., "Isotope Tracers for Tracking Groundwater Recharge." California Water Reuse Association, Artificial Water Recharge Workshop, Newport Beach, CA, April 5, 1997.

Hudson, G.B., "The Xe-124 Water Infiltration Experiment at Anaheim Lake." Santa Ana River Water Quality and Health Effects Study, Orange County Water District, Fountain Valley CA, June 10-11, 1997.

INF / TFA

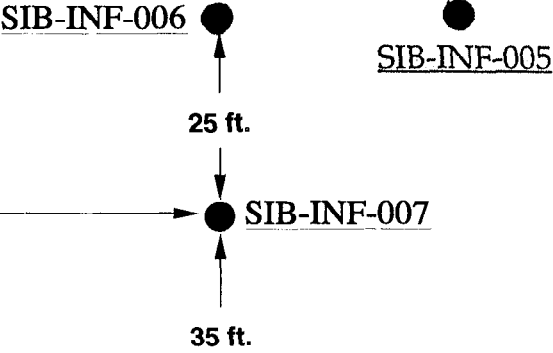
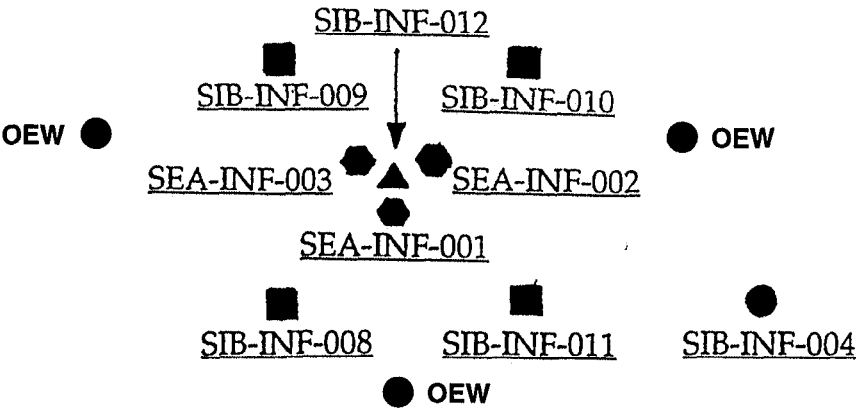
Vasco Rd.

Fence

Gate

MW-619

● Outer ERT Well (OEW)



Fence

East Ave.

Joint Inversion of Geophysical Data for Site Characterization and Restoration Monitoring
(Summary Report on Progress in FY97 for EMSP Project 55411, TTP No. SF2-7-SP-22)

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Research Objective

The purpose of this project is to develop a computer code for joint inversion of seismic and electrical data, to improve underground imaging for site characterization and remediation monitoring. The computer code developed in this project will invert geophysical data to obtain direct estimates of porosity and saturation underground, rather than inverting for seismic velocity and electrical resistivity or other geophysical properties. This is intended to be a significant improvement in the state-of-the-art of underground imaging, since interpretation of data collected at a contaminated site would become much less subjective. Potential users include DOE scientists and engineers responsible for characterizing contaminated sites and monitoring remediation of contaminated sites.

Research Statement

Effective in-situ remediation requires a knowledge of subsurface porosity, permeability, and fluid saturation. Only after the site has been characterized can the clean-up begin. Using geophysical techniques to image the subsurface is much cheaper and less invasive than drilling many sampling wells. Electrical methods have usually been used for environmental applications, but recent advances in high-resolution crosswell seismic methods (e.g., Harris et al., 1995) suggest that combined electrical and seismic techniques could be a powerful tool for imaging the shallow subsurface.

Surface and borehole geophysical data have been used for a number of years for site characterization and clean-up monitoring (e.g., Ramirez et al., 1993, 1995; Wilt et al., 1995a,b) and monitoring steam-flooding in hydrocarbon reservoirs (e.g., Harris, 1988; Mathisen et al., 1995), but these data may only indirectly measure the site structure and fluid flow parameters that control the storage and movement of subsurface fluids. The current practice in geophysics is to interpret a single geophysical data set to obtain an image of a single geophysical parameter, such as seismic velocity or electrical resistivity. The geologic parameters of interest (i.e., the permeability, porosity, and fluid distribution) are usually estimated by overlaying a series of these geophysical images. Current estimation techniques are very subjective, and geologic parameters are not obtained directly. Current practices also do not exploit the complementary capabilities of seismic and electrical methods. Seismic methods are best for resolving subsurface structure and porosity (e.g., Lines et al., 1993; Mathisen et al., 1995), whereas electrical methods are preferred for identifying fluids, saturation, and permeability (e.g., Wilt et al., 1995a,b).

The goal of our project is to develop a code for joint inversion of seismic and electrical data. We will invert these data to obtain direct estimates of the porosity and saturation, rather than inverting for seismic velocity and electrical resistivity. Our method exploits the complementary nature of seismic and electrical measurements, and leads to an objective estimate of the geological and fluid flow parameters that are of most interest. This approach provides a dual benefit to environmental site assessment. First, it provides a powerful set of tools for jointly inverting geophysical data; and secondly, it provides a common platform for visualizing the results. No longer will it be necessary to overlay disparate images to look for common anomalies. Instead of comparing multiple images of electrical conductivity and seismic velocity for site information, we will examine single images of porosity and saturation that are derived from the geophysical data.

The ultimate objective of this work is to use geophysical and well-test data to provide accurate information about porosity, saturation, and permeability between wells. In this three-year project, we use a multi-phase approach consisting of theoretical and numerical

code development, laboratory investigations, testing on available laboratory and borehole geophysics data sets, and a controlled field experiment, to develop practical tools for joint electrical and seismic data interpretation. This report describes progress made in the first year, including theoretical development of physical properties relationships and laboratory investigations of electrical and elastic properties of sand-clay mixtures. The schedule of this project is as follows. In the first year, investigators perform laboratory measurements of elastic and electrical properties of sand-clay mixtures containing various fluids. Investigators also develop methods of relating measurable geophysical properties to porosity and saturation by using rock physics theories, geostatistical, and empirical techniques together with available laboratory measurements. In the second year, investigators finish any necessary laboratory measurements and apply the methods developed in the first year to invert available borehole log data to predict measured properties of cores and sediments from a borehole. Investigators refine the inversion code in the third year and carry out a field experiment to collect seismic and electrical data. Investigators then use the inversion code to invert the field data to produce estimates of porosity and saturation in the field area where the data were collected.

This report summarizes progress made in the first year of this three-year project. For more information on work planned for the second and third years, and for additional technical details, see either the original proposal submitted to the EMSP program or see the world-wide web homepage that we have created for this project, at the URL

<http://www-ep.es.llnl.gov/www-ep/esd/expgeoph/Berge/EMSP/>

Research Progress

Development of the joint inversion code requires developing algorithms relating geophysical data to porosity and saturation. Work done in the first year of this project provides the basis for developing and testing the inversion code on borehole and field data in the second and third years of the project. We are developing the necessary algorithms using a flexible approach that will allow us to assess the relative usefulness of geostatistical methods, empirical techniques commonly used in borehole geophysics interpretation (e.g., Archie, 1942, Wyllie et al., 1956, 1958; Waxman and Smits, 1968), and rock physics theories (see Berryman, 1995 for a review) that describe how elastic wave velocities and electrical conductivities depend on porosity and saturation in porous materials having different microgeometries. Much of the code for the theoretical analysis already exists in various forms (e.g., Cheng, 1978, Berge et al., 1992, 1993, 1995, Berryman, 1995, Berryman and Berge, 1996). Existing effective medium theory algorithms that were developed for use with consolidated materials at moderately high pressure conditions must be modified for application to the near surface environment. Empirical methods that were mainly developed for consolidated materials and oil industry applications may or may not be effective for environmental applications. In order to test these different techniques, we have made an exhaustive search of the marine geophysics, civil engineering, soil mechanics, exploration geophysics, and environmental geophysics literature to find available information on rock properties measurements for unconsolidated sands and clays at low pressures (i.e. shallow depths). We have compiled a database containing elastic properties data for unconsolidated sediments that we will use to modify and test the necessary algorithms for relating elastic properties to porosity and saturation for dry and fully saturated sediments. (A representative portion of this database was included as an appendix to the FY97 progress report submitted to the EMSP at the end of FY97, but will not be included here because of space considerations.)

Since limited information is available for unconsolidated sediments at low pressures appropriate for the near-surface, particularly for sediments containing clays, we have made our own laboratory measurements for unconsolidated sand-clay mixtures and are in the process of reducing and interpreting both elastic and electrical properties data. Our laboratory equipment allows us to measure porosities and permeabilities as well as geophysical properties. This provides the needed information for developing relationships between geophysical properties and the hydrogeologic parameters that are most useful for environmental applications. (We will complete our laboratory measurements in the second year, concurrently developing and testing the inversion algorithm.)

Diagrams of our measurement apparatus and some preliminary results are included in the Experimental Results subsection below. Our preliminary results suggest that microstructure controls the geophysical properties. Thus microstructure assumptions used in empirical or theoretical methods may be the determining factor for which methods are most useful for developing the algorithms that relate geophysical properties to porosity and saturation. In addition to the work on geophysical properties data, we have made progress in developing rock physics theories for estimating rock and sediment properties for mixtures such as unconsolidated sands and clays that may be dry or fully saturated. This progress is described in the Progress on Theories subsection later in this report.

Experimental Results

We have been conducting a series of electrical and elastic properties measurements on a limited number of sand-clay mixtures, using filtered, deionized water, tap water, and KCl brines of a few different salinities for the pore fluids. Fluid conductivities were measured using an Omega water analyzer. Dry and fully saturated samples were used, to simplify the velocity measurements since partial saturation introduces a significant degree of complexity to the problem. We have been investigating the effects of different clays such as kaolinite, bentonite, and a natural clay-rich soil called Alligator clay. We have used various mixing techniques to construct the sand-clay samples, since the microgeometry is a critical factor affecting measured elastic and electrical properties.

Future work will include measurements on contaminated soils that we have obtained from two boreholes at an LLNL site, as well as characterizing our samples using x-ray computed tomography to obtain microstructural information such as estimates of water content and indications of clay degradation and interaction with DNAPL pore fluids.

Electrical Properties

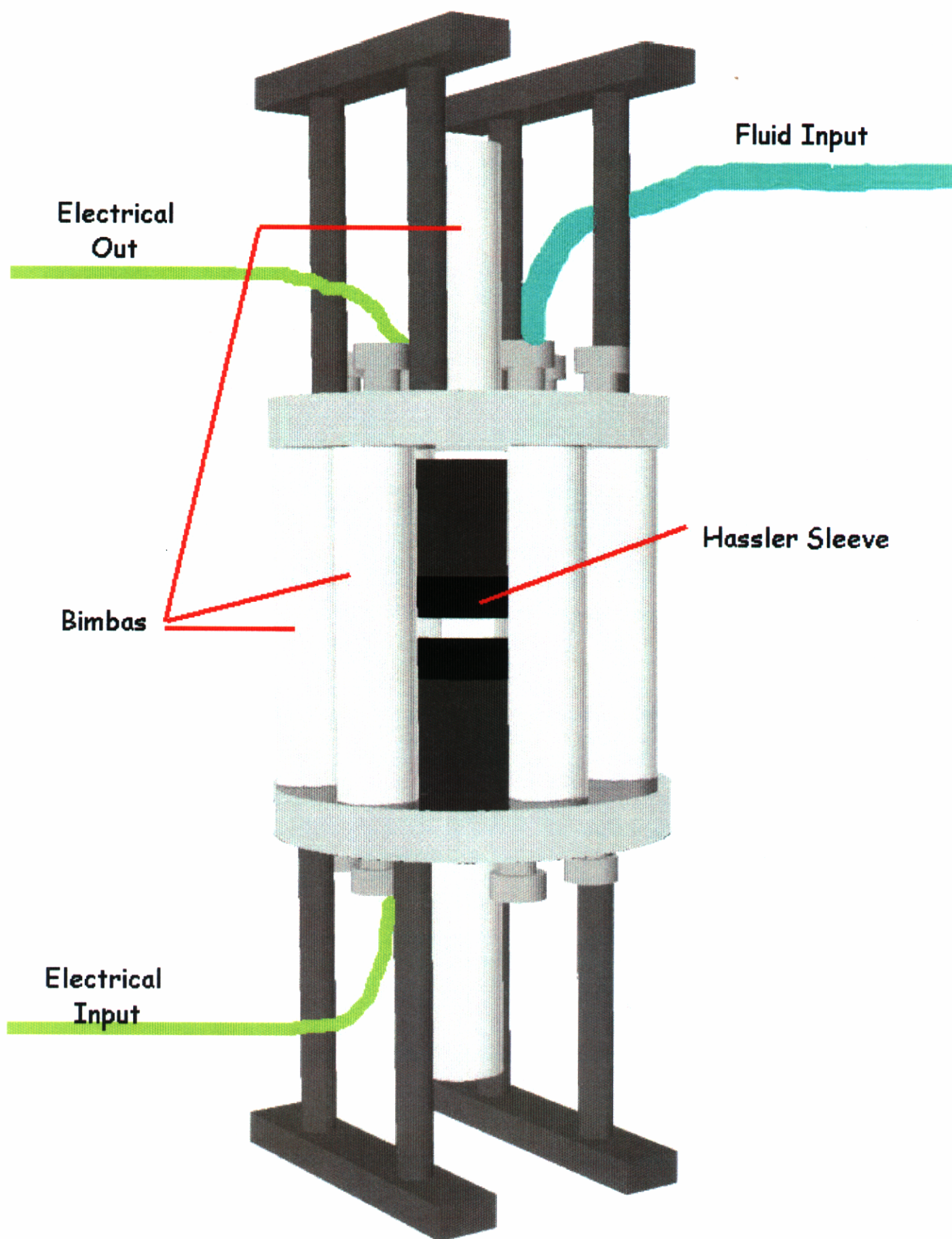
For the electrical properties measurements, we have made complex resistivity measurements over a large range of frequencies so that we can analyze the contributions of different conduction mechanisms to the overall electrical properties of a given sample. Complex resistivity measurements are often useful in determining the role of specific conduction mechanisms such as clay surface conduction (e.g., Olhoeft, 1985; Olhoeft and King, 1991; Garrouch and Sharma, 1994). Non-linear phenomena may be produced in clay-bearing rocks and sediments by cation exchange, surface conduction, and clay-organic reactions (e.g., Olhoeft, 1985; Ramirez et al., 1993).

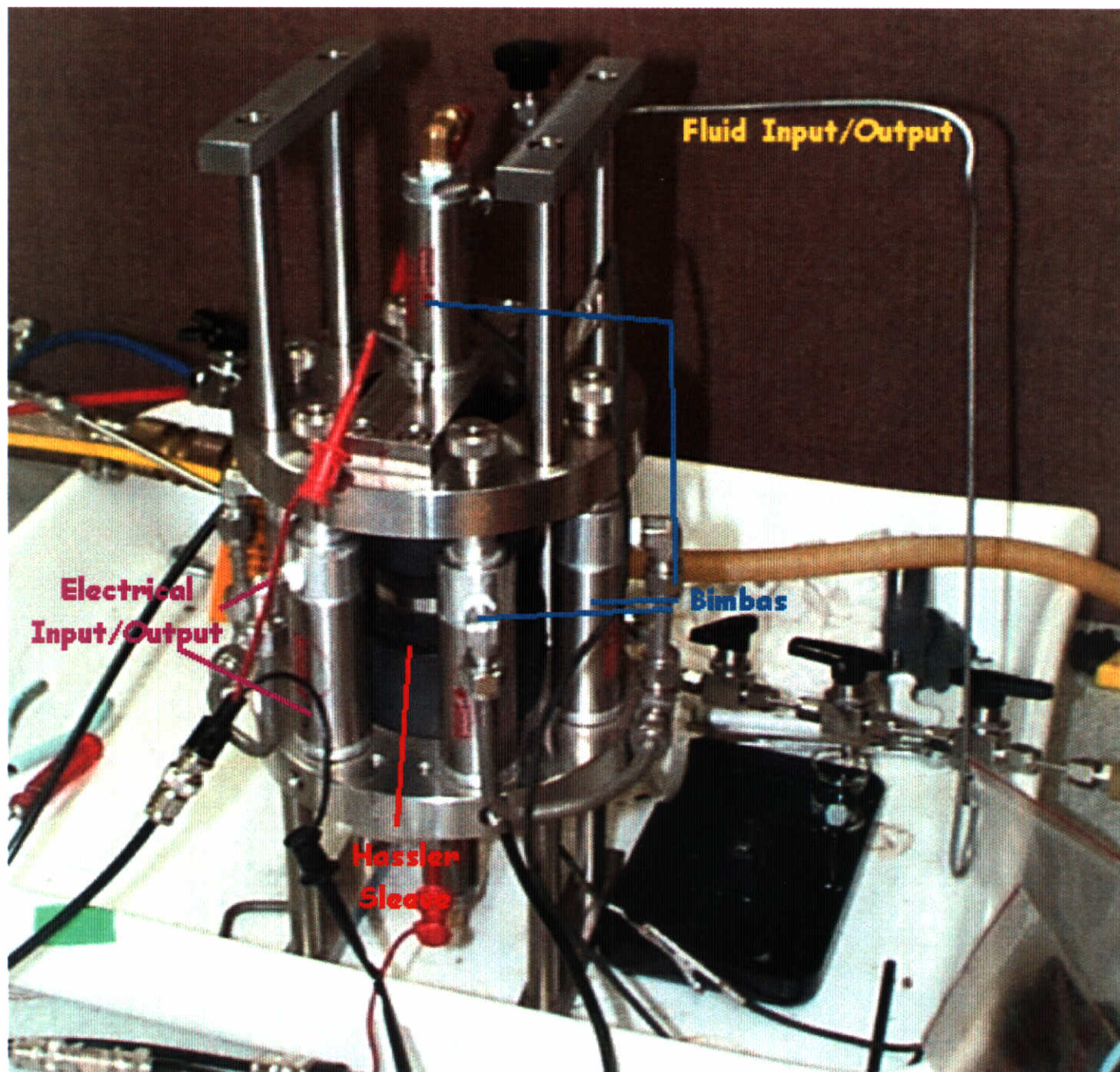
One of our component systems has a function generator to supply current at frequencies between 0.001 and 100,000 Hz, and uses an EGG lock-in amplifier. Additional impedance measuring systems available in the LLNL Experimental Geophysics laboratory extend the range of frequencies we can use for our measurements. These three other systems have frequency ranges of 100 to 100,000 Hz and 10 Hz to 1 MHz for two HP LCR meter.

systems, and 0.00001 to 100000 Hz for an EGG electrochemical impedance system. Figures 1 and 2 show a schematic diagram and a photograph of part of the apparatus used for electrical measurements.

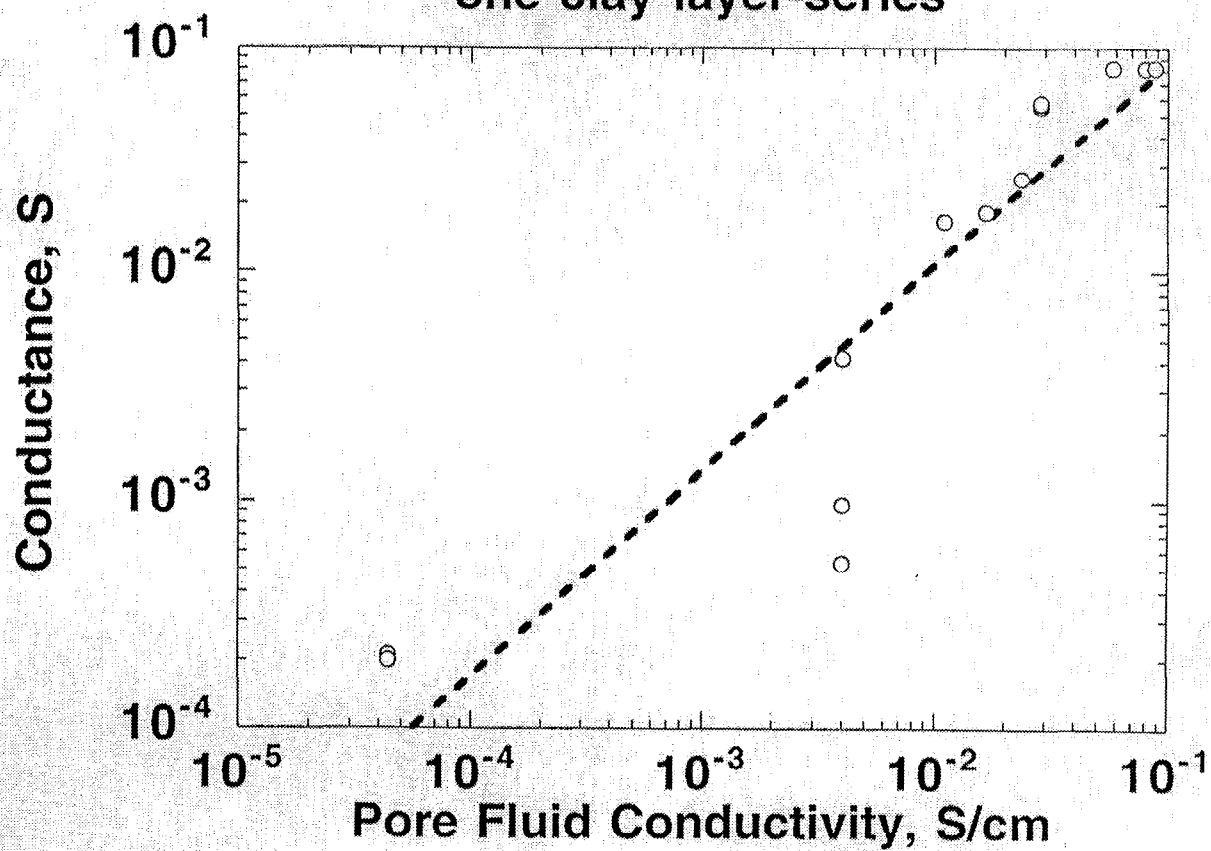
We are still in the process of reducing and analyzing the electrical properties results. Figures 3 through 8 show examples of some preliminary results for the electrical properties measurements.

We are currently experimenting with other types of electrodes, to reduce some of the sources of measurement uncertainty. Previous measurements were made using platinum wires. We are experimenting with Ag wires that we are trying to react with NaCl or KCl solution to form AgCl on the wire. This should eliminate some electrode polarization problems. We are making progress on sample porosity and permeability measurements for the electrical apparatus. Presently we are using separate equipment for elastic and electrical properties measurements instead of using a single apparatus, because of difficulties with the measurement techniques interfering with each other and causing large uncertainties in results. We are using samples that are matched as closely as possible for the sand-clay mixtures, with respect to saturation, porosity, clay type, flocculation of clays, etc. Elastic wave velocity measurements will be discussed below, after the figures showing electrical measurements.

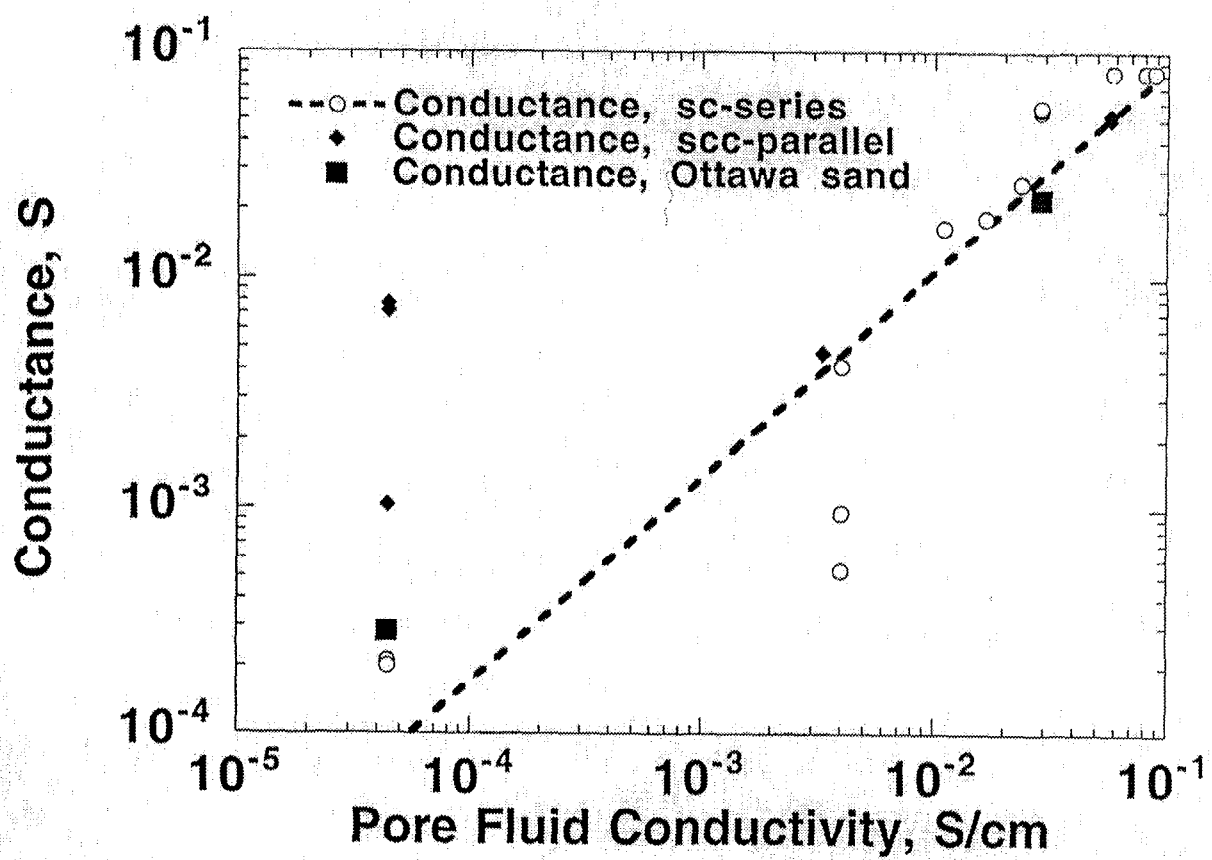




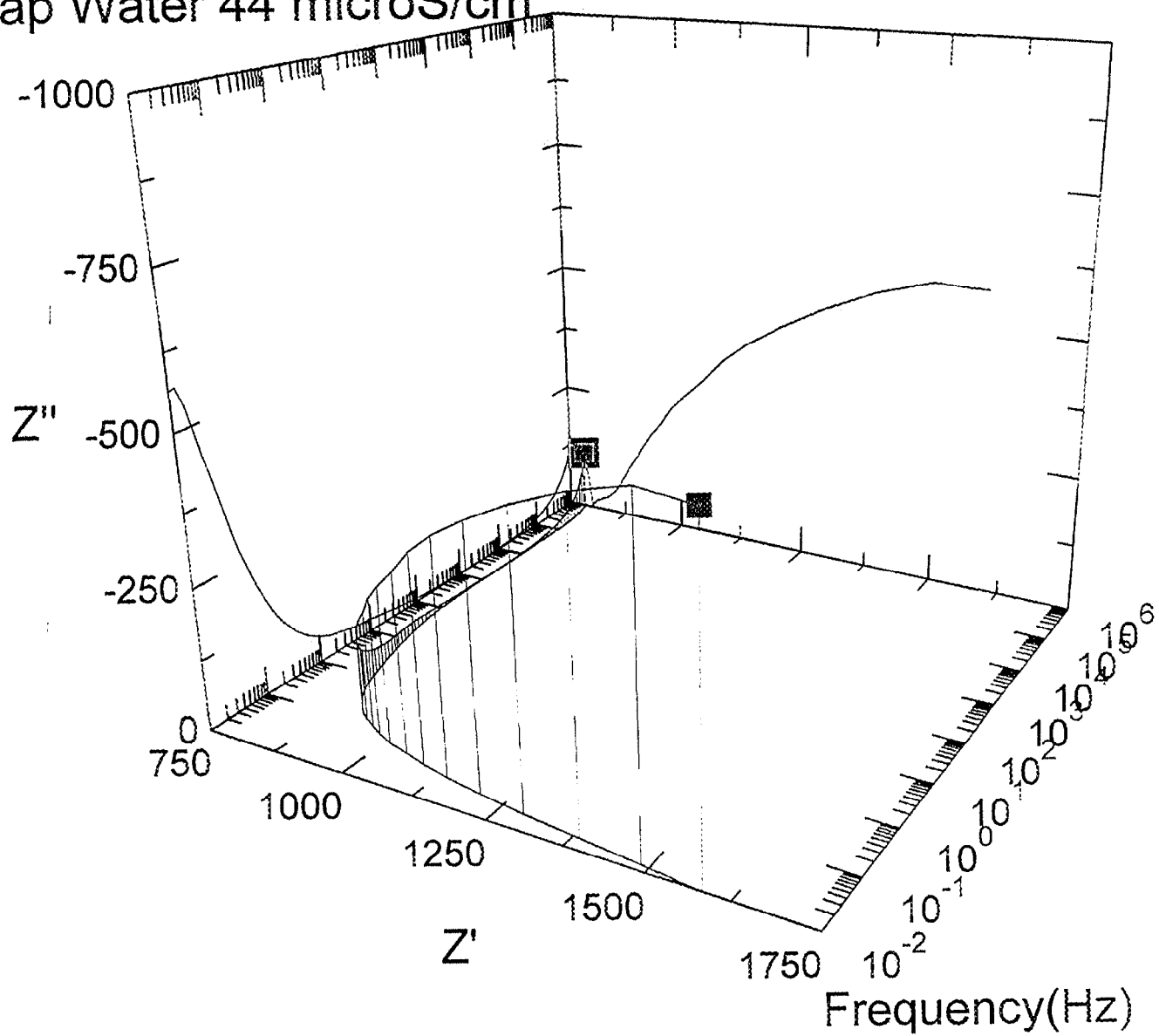
Ottawa Sand/Alligator Clay
one clay layer-series

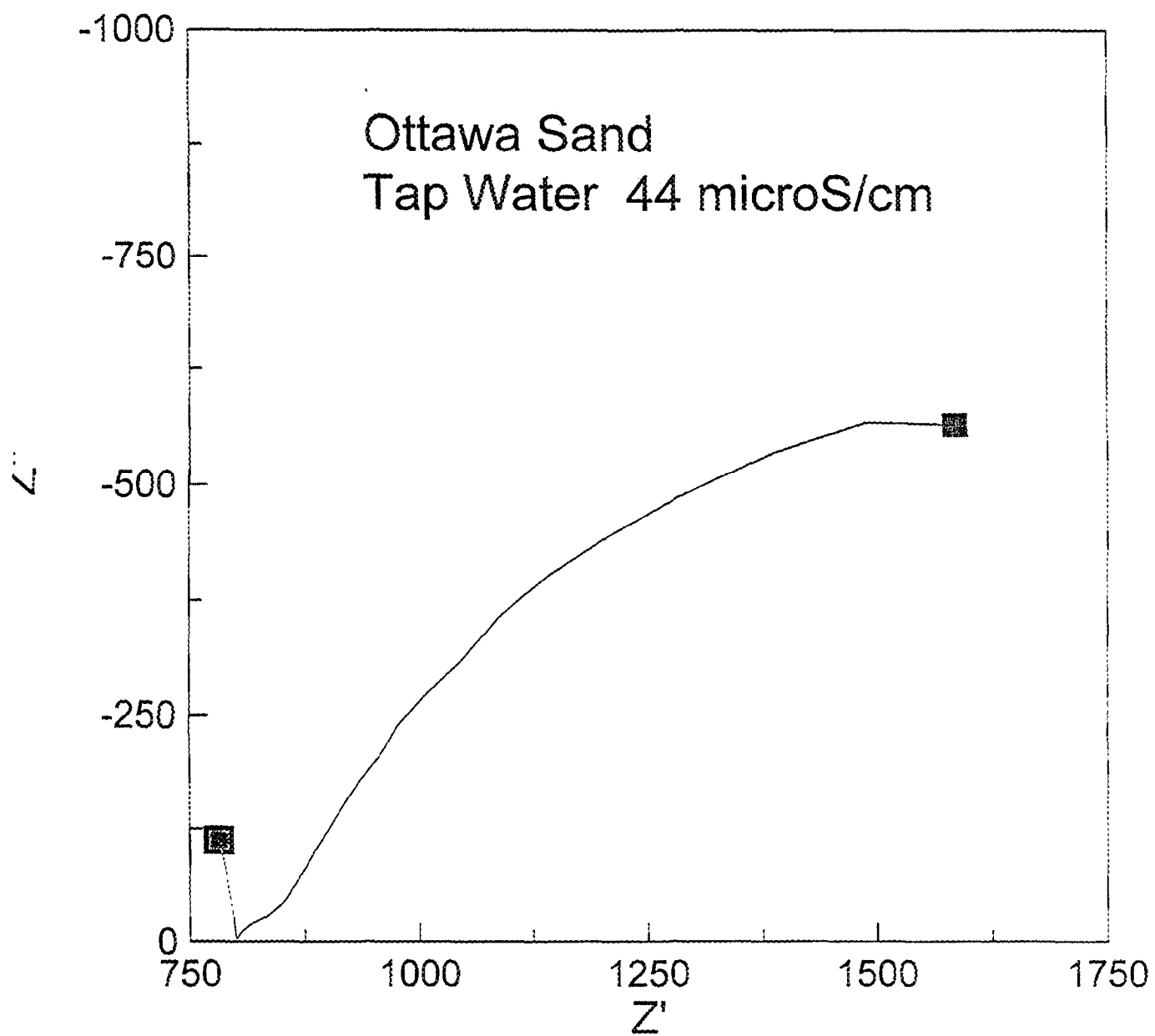


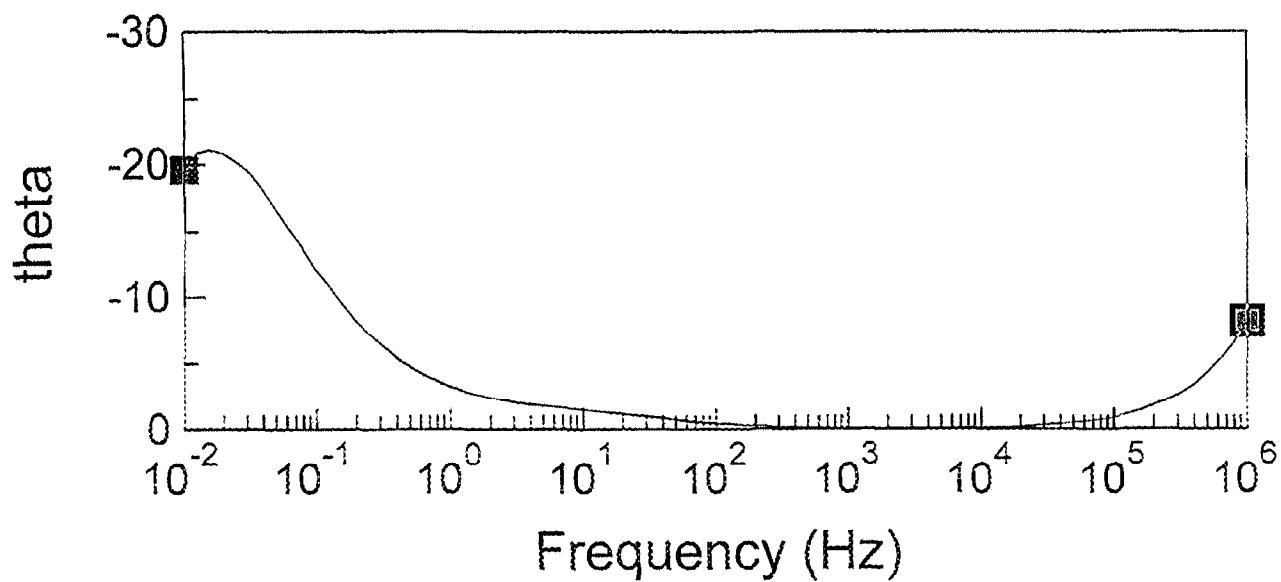
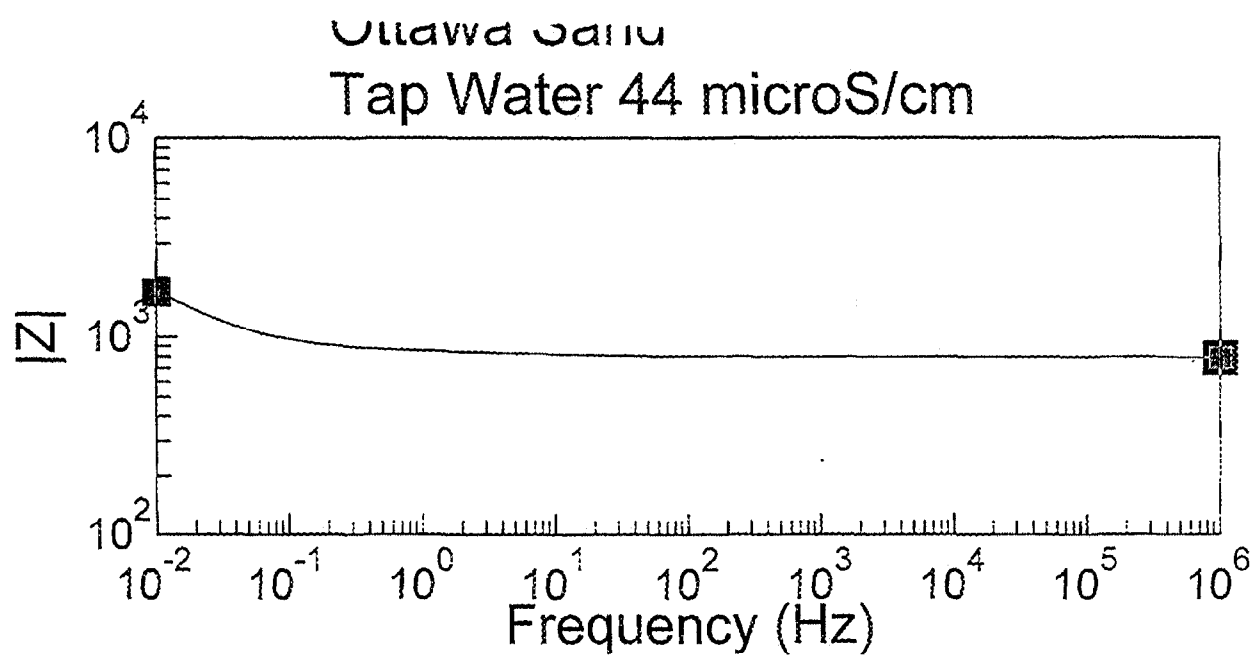
Conductance of Sand and Sand-Clay Mixtures



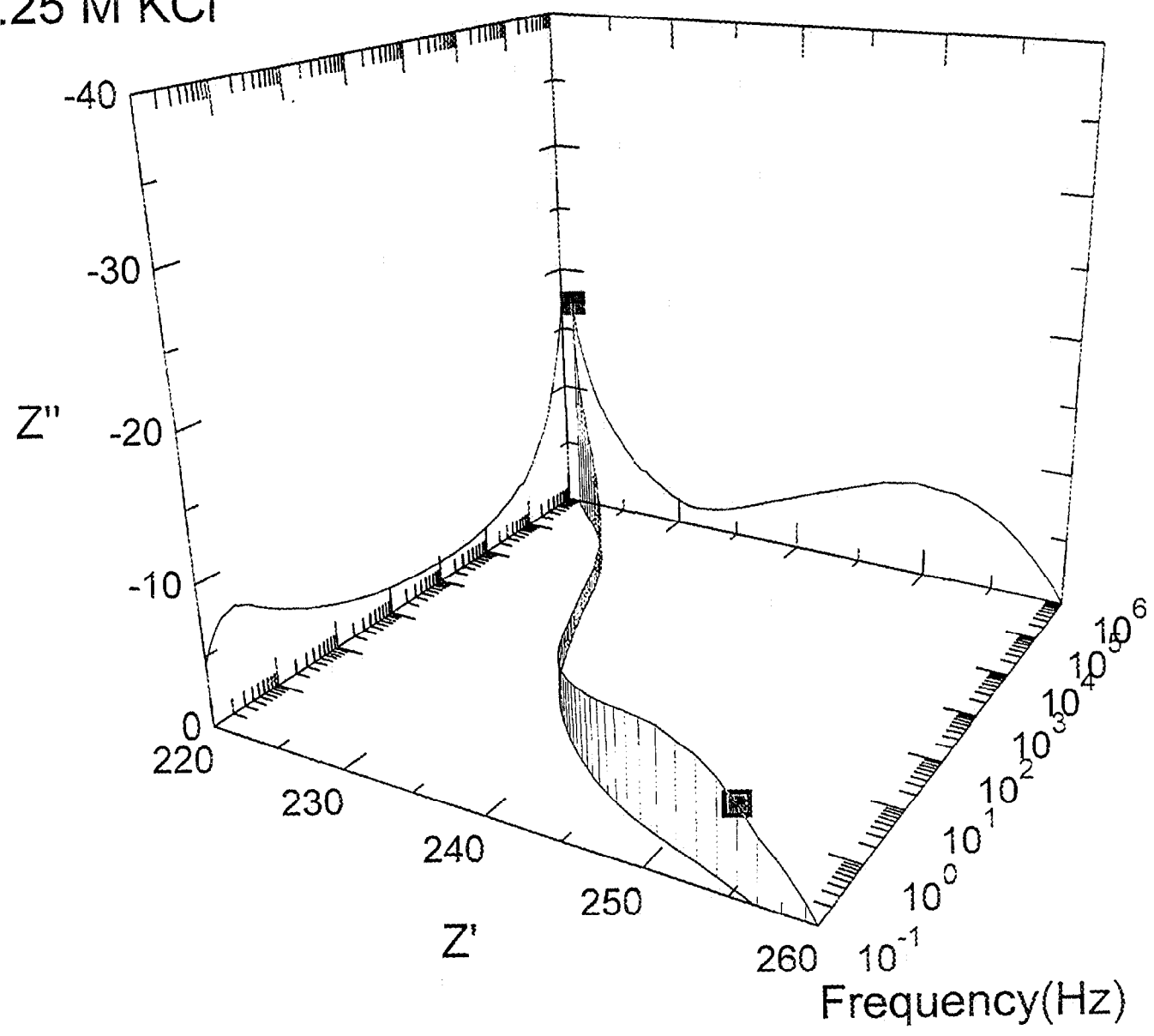
Ottawa Sand
Tap Water 44 microS/cm







Sample sccsp5
0.25 M KCl



Captions for Figures 1 through 8:

Figure 1. 3D image of apparatus used to make electrical measurements on samples. The two-inch diameter sample is placed inside the Hassler sleeve, which applies confining pressure. Axial pressure is applied by the pneumatic cylinders around the perimeter and on the top and bottom. The fluid tube allows continuous input of various fluids. The electrical coaxial cables are used for electrical conductivity measurements.

Figure 2. Photograph showing experimental setup for electrical measurements. The electrical measurements are made as a function of frequency between 1 MHz and 1 mHz for each sample. The four-electrode method is used. The metallic frits serve as the end electrodes and the wire loops work as the inner, voltage measuring electrodes. The use of different saturating fluids (with differing electrical conductivities) helps to determine the dominant conduction pathways through the sample.

Figure 3. Sample conductance (1/resistance) vs. fluid conductivity (in siemens/cm) for a mixture of Ottawa sand and Alligator clay. There is one layer of clay. It is in series electrically; that is, the layer is parallel to the frit electrodes. The line is a fit that shows a roughly linear dependence on a log-log plot.

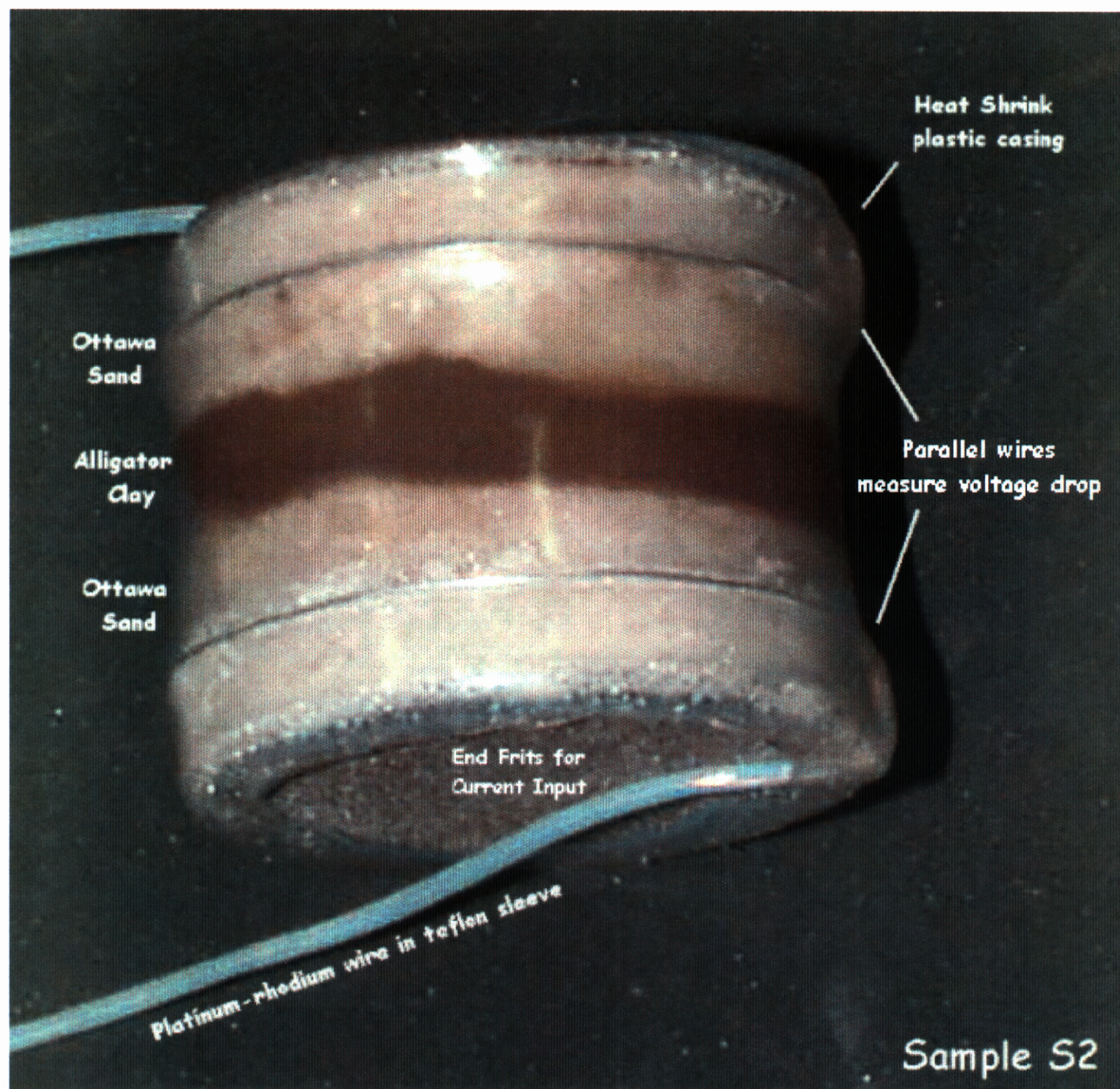
Figure 4. Similar to Figure 3, with the addition of a few data points from other configurations. sc-series is the same as Figure 3. scc-parallel is a clay layer that is in parallel electrically; that is, perpendicular to the electrodes. Ottawa sand is a strictly sand sample. The sand sample and series sample are essentially the same. The series clay layer has very little effect on conductivity. What is different is the parallel clay layer sample, which is more conductive at lower fluid conductivities. (More study should be done before any strong conclusions are drawn from this.)

Figure 5. This shows the frequency-dependent electrical properties of a sample of 100 percent Ottawa sand and tap water (44 microS/cm conductivity).

Figure 6. These are the same data as in Figure 5, plotted slightly differently. Figure 6 is the familiar -Imag. Z vs. Real Z (impedance). Compare also to Figure 7.

Figure 7. These are the same data as in Figures 5 and 6, plotted slightly differently. Figure 7 shows impedance magnitude and phase as a function of frequency.

Figure 8. This figure shows the frequency dependence of a sample with clay layers in parallel (electrically). It was saturated with 0.25 M KCl solution (28.6 mS/cm conductivity). This can be contrasted with the response in Figures 5 and 6.



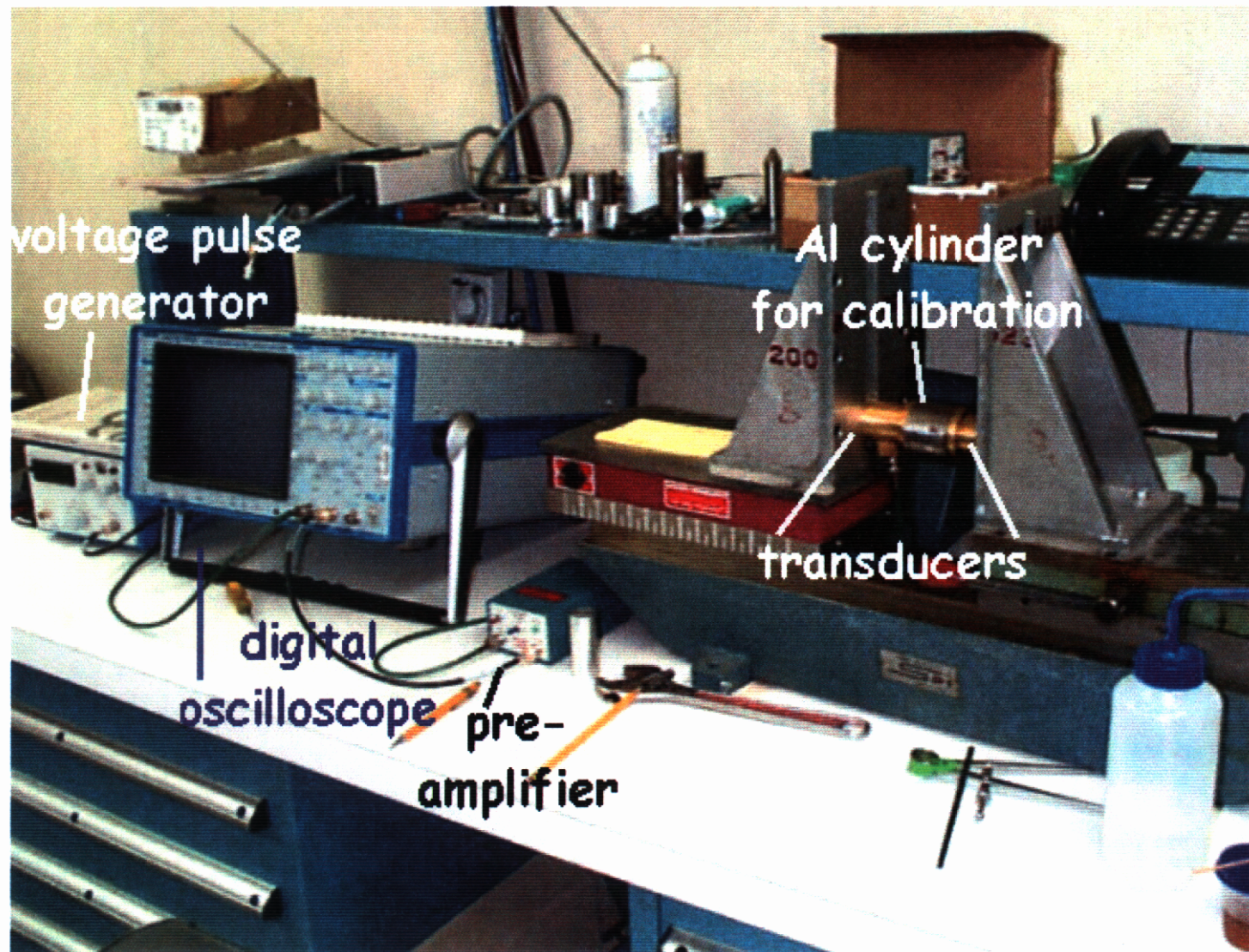
Elastic Wave Velocities

We have measured both compressional- and shear-wave velocities for various sand-clay mixtures and pure sand samples, at ambient pressure conditions as well as using small (about 1 to 15 psi) known axial loads on the samples. We are in the process of reducing and analyzing these data.

In general, we find that our measured velocities are similar to values found in the literature, where available. For example, we find velocities of about 500 m/s for compressional waves in Ottawa sand at low pressures. Our database includes values of about 400 m/s to 600 m/s for similar sand under similar conditions (Rao, 1966), and values of about 300 m/s to 400 m/s for similar sand at pressures of 2, 5, and 25 psi (Whitman, 1966). Consolidated sandstones and unconsolidated sands at higher pressures (e.g., 1500 psi) have much higher velocities, near 1500 m/s (Wyllie et al., 1956; Domenico, 1976). We measured shear wave velocities near 300 m/s in our dry sand sample, at low axial pressure (near 2 psi). We did not find any low-pressure measurements of shear velocities for unconsolidated sediments on land in the literature, but marine sediments are known to have similar shear velocities (e.g., Berge et al., 1991).

Our preliminary results indicate that microstructure controls the velocities, and that clay microstructure is particularly important. We are investigating the effects of flocculation and de-flocculation on mechanical properties, and submitted an abstract on this topic for presentation at the 1997 Fall Annual Meeting of the American Geophysical Union (Bonner et al., 1997).

Figure 9 shows an example of one of the samples used for separate elastic wave velocity and electrical properties measurements. (We have since redesigned sample holders for velocity measurements to improve signal quality, and are no longer using the same sample for both sets of measurements.) Figure 10 shows a photograph of the apparatus used to measure compressional- and shear-wave velocities.



Captions for Figures 9 and 10:

Figure 9. Sample design showing construction. The double-layered plastic casing is rigid enough to hold the sample intact and protect its structure, but not rigid enough to affect elastic wave velocity measurements. The sample shown is primarily made up of Ottawa sand with an approximately 1 cm layer of Alligator clay in the center. The transparent casing allows researchers to monitor the condition of the sample to insure that the electrode wires remain parallel, and the internal structure does not change. (This sample design was later changed to improve elastic wave velocity measurement results.)

Figure 10. Photograph showing experimental setup for elastic wave velocity measurements. Aluminum and steel cylinders of varying lengths and diameters were used to calibrate the apparatus, and find the travel time through the transducer assembly. Various sets of transducers are used.

Progress on Theories

In FY97, three papers on theoretical methods for estimating properties of porous media were completed (Berryman and Pride, 1997; Dvorkin et al., 1997; Pride and Berryman, 1997). These abstracts from these papers are presented below.

Abstract from Volume Averaging, Effective Stress Rules, and Inversion for Microstructural Response of Multicomponent Porous Media (J. G. Berryman and S. R. Pride, International Journal of Solids and Structures, in press, 1997)

A general volume-averaging technique is used to derive equations satisfied by the average scalar stresses and strains in multicomponent porous rock. The resulting equations are combined with general thought experiments to produce the effective-stress rules that determine the volumetric changes of the rock induced by changes in the confining and fluid pressures. The composite porous material specifically treated is an isotropic mixture of two Gassmann materials. Two distinct cases are considered depending on whether the grains at the interface between the Gassmann materials are either 1) welded together (no cracks can open between the two constituents) or 2) nonwelded (cracks can open). The effective-stress laws determine not only the overall volumetric changes of a given sample (i.e., changes in sample volume, total pore volume, and fluid-mass content), but determine as well the changes within each Gassmann component individually. This additional level of detail achieved in the analysis is referred to as the inversion for the microstructural response. In the nonwelded case, the effective-stress law relating the variation of crack porosity with macroscopic changes in confining and fluid stress can be used to determine optimum strategies for increasing fracture/crack porosity with applications to reservoir production analysis.

Abstract from Effective Moduli of Particulates with Elastic Cement (J. Dvorkin, M. Le Ravalec, J. Berryman, and A. Nur, submitted to Mechanics of Materials, 1997)

We give an approximate method for calculating the effective elastic moduli of a close random pack of identical elastic spheres whose pore space is partially or completely filled with elastic cement. To construct the solution we start with the uncemented pack and add small amounts of cement uniformly at every grain contact. The effective moduli of such an aggregate depend on those of the grains and cement (which are, generally, different), and on the amount of cement. Moduli for grain/cement mixtures are available from the contact cementation theory. Next we introduce an isotropic elastic body with void inclusions (e.g., spherical) whose porosity is the same as the porosity of the pack with contact cement. The moduli of the matrix are as yet unknown. We find them by assuming that the effective moduli of the elastic body with inclusions are equal to those of the pack with contact cement. Then an appropriate effective medium theory (e.g., self-consistent or differential effective medium approximation) provides two equations for the bulk and shear moduli of the matrix. Finally, we use the chosen effective medium theory to calculate the moduli of the elastic body with the matrix thus defined whose inclusions are now filled with the cement. We assume that these are also the moduli of the pack whose pore space is completely filled with the cement. To calculate the elastic moduli of the pack whose pore space is partially filled with the cement, we assume that they are those of the elastic body with the matrix thus defined and with two types of inclusions -- void and filled with cement. The porosities of this body and of the cemented pack are the same. This result gives one solution to a general and previously unresolved effective medium problem of contacting elastic inclusions embedded in an elastic matrix. It provides a transition from high-porosity cemented to completely cement-filled granular materials. The solution

accurately predicts the compressional elastic modulus (the product of the bulk density and P-wave velocity squared) from wave-propagation experiments on cemented glass beads and natural rocks.

Abstract from Connecting Theory to Experiment in Poroelasticity (S. R. Pride and J. G. Berryman, International Journal of the Mechanics and Physics of Solids, in press, 1997)

The variables controlled and measured in elastostatic laboratory experiments (the volume changes, shape changes, and confining pressures) are exactly related to the appropriate variables of poroelastic field theory (the gradients of the volume-averaged displacement fields and the volume-averaged stresses). The relations between the laboratory and volume-averaged strain measures require the introduction of a new porous-material geometrical term. In the anisotropic case, this term is a tensor that is related both to the presence of porosity gradients and to a type of weighted surface porosity. In the isotropic case, the term reduces to a scalar and depends only on the surface-porosity parameter. When this surface-porosity parameter is identical to the usual volume porosity, the relations initially proposed by Biot and Willis are recovered. The exact statement of the poroelastic strain-energy density is derived and is used to relate the moduli measured in laboratory experiments to the moduli of poroelastic theory. Only two restrictions are placed on the materials being treated: 1) the fluid is homogeneous in each sample and 2) the material possesses a rigidity. However, the entire work is limited to linear deformations and long (relative to sample size) wavelengths of applied stress.

Summary of Accomplishments

Built, tested, and used laboratory apparatus for measuring elastic wave velocities in unconsolidated sediments (sand-clay mixtures).

Modified, tested, and used laboratory apparatus for measuring complex electrical conductivity in unconsolidated sediments.

Conducted extensive search of engineering and earth science literature and created a database containing elastic velocity data for unconsolidated sediments.

Extended and developed rock physics theories for estimating properties of unconsolidated sediments.

Created world-wide web home page for this project.

Submitted papers for publication in peer-reviewed journals and presentation at a prestigious geophysics conference.

Acknowledgments

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Papers and Abstracts

The following papers, abstract, and world-wide web home page were produced in FY97 for this EMSP project:

Berge, P. A., and C. D. Rowe, 1997, Joint Inversion of Geophysical Data for Site Characterization and Restoration Monitoring, World-Wide Web Home Page, UCRL-MI-128343, Lawrence Livermore National Laboratory, Livermore, CA.

Berryman, J. G., and S. R. Pride, 1997, Volume averaging, effective stress rules, and inversion for microstructural response of multicomponent porous media: *Int. J. Sol. Struct.*, in press.

Bonner, B. P., D. J. Hart, P. A. Berge, and C. M. Aracne, 1997, Influence of chemistry on physical properties: Ultrasonic velocities in mixtures of sand and swelling clay (abstract): presented at the Fall Meeting of the American Geophysical Union, San Francisco, California, December 8-12, 1997.

Dvorkin, J., M. Le Ravalec, J. Berryman, and A. Nur, 1997, Effective moduli of particulates with elastic cement: submitted to *Mechanics of Materials*.

Pride, S. R., and J. G. Berryman, 1997, Connecting theory to experiment in poroelasticity: *J. Mech. Phys. Sol.*, in press.

References

Archie, G. E., 1942, The electrical resistivity log as an aid in determining some reservoir characteristics: *Trans. AIME*, 146, 54-62.

Berge, P. A., S. Mallick, G. J. Fryer, N. Barstow, J. A. Carter, G. H. Sutton, and J. I. Ewing, 1991, In situ measurement of transverse isotropy in shallow-water marine sediments: *Geophys. J. Int.*, 104, 241-254.

Berge, P. A., G. J. Fryer, and R. H. Wilkens, 1992, Velocity-porosity relationships in the upper oceanic crust: Theoretical considerations: *J. Geophys. Res.*, 97, 15239-15254.

Berge, P. A., J. G. Berryman, and B. P. Bonner, 1993, Influence of microstructure on rock elastic properties: *Geophys. Res. Lett.*, 20, 2619-2622.

Berge, P. A., B. P. Bonner, and J. G. Berryman, 1995, Ultrasonic velocity-porosity relationships for sandstone analogs made from fused glass beads: *Geophysics*, 60, 108-119.

Berge, P. A., and C. D. Rowe, 1997, Joint Inversion of Geophysical Data for Site Characterization and Restoration Monitoring, World-Wide Web Home Page, UCRL-MI-128343, Lawrence Livermore National Laboratory, Livermore, CA.

Berryman, J. G., 1995, Mixture theories for rock properties, in Ahrens, T. J., Ed., *Rock Physics and Phase Relations, A Handbook of Physical Constants*, Am. Geophys. Union, Washington, D.C., 205-228.

Berryman, J. G., and P. A. Berge, 1996, Critique of two explicit schemes for estimating elastic properties of multiphase composites: *Mechanics of Materials*, 22, 149-164.

Berryman, J. G., and S. R. Pride, 1997, Volume averaging, effective stress rules, and inversion for microstructural response of multicomponent porous media: *Int. J. Sol. Struct.*, in press.

Bonner, B. P., D. J. Hart, P. A. Berge, and C. M. Aracne, 1997, Influence of chemistry on physical properties: Ultrasonic velocities in mixtures of sand and swelling clay (abstract): presented at the Fall Meeting of the American Geophysical Union, San Francisco, California, Dec. 8-12, 1997.

Cheng, C. H., 1978, Seismic velocities in porous rocks: direct and inverse problems: Ph.D. thesis, Mass. Inst. of Technol., Cambridge, Mass.

Domenico, S. N., 1976, Effect of brine-gas mixture on velocity in an unconsolidated sand reservoir: *Geophysics*, 41, 882-894.

Dvorkin, J., M. Le Ravalec, J. Berryman, and A. Nur, 1997, Effective moduli of particulates with elastic cement: submitted to *Mechanics of Materials*.

Garrouch, A. A., and M. M. Sharma, 1994, The influence of clay content, salinity, stress, and wettability on the dielectric properties of brine-saturated rocks: 10 Hz to 10 MHz: *Geophysics*, 59, 909-917.

Harris, J. M., 1988, High frequency cross-well seismic measurements in sedimentary rocks: 58th Annual Internat. Mtg., Soc. Expl. Geophys., Expanded Abstracts, 147-150.

Harris, J. M., R. C. Nolen-Hoeksema, R. T. Langan, M. Van Schaack, S. K. Lazaratos, and J. W. Rector III, 1995, High-resolution crosswell imaging of a west Texas carbonate reservoir: Part 1-Project summary and interpretation: *Geophysics*, 60, 667-681.

Lines, L. R., M. Miller, H. Tan, R. Chambers, and S. Treitel, 1993, Integrated interpretation of borehole and crosswell data from a west Texas field: *The Leading Edge*, 12, 13-16.

Mathisen, M. E., A. A. Vassiliou, P. S. Cunningham, J. Shaw, J. H. Justice, and N. J. Guinzy, 1995, Time-lapse crosswell seismic tomogram interpretation: Implications for heavy oil reservoir characterization, thermal recovery process monitoring, and tomographic imaging technology: *Geophysics*, 60, 631-650.

Olhoeft, G. R., 1985, Low-frequency electrical properties: *Geophysics*, 50, 2492-2503.

Olhoeft, G. R., and T. V. V. King, 1991, Mapping subsurface organic compounds noninvasively by their reactions with clays: *Proc. of the 4th Toxic Substances Hydrology Tech. Mtg.*, USGS, 552-557.

Pride, S. R., and J. G. Berryman, 1997, Connecting theory to experiment in poroelasticity: *J. Mech. Phys. Sol.*, in press.

Ramirez, A., W. Daily, D. LaBrecque, E. Owen, and D. Chesnut, 1993, Monitoring an underground steam injection process using electrical resistance tomography: *Water Resources Res.*, 29, 73-87.

Ramirez, A. L., W. D. Daily, and R. L. Newmark, 1995, Electrical resistance tomography for steam injection monitoring and process control: *J. Env. Eng. Geophys.*, 0, 39-51.

Rao, H. A. B., 1966, Wave velocities through partially saturated sand-clay mixtures: Massachusetts Institute of Technology Dept. of Civil Engineering Research Report, R66-13.

Waxman, M. H., and J. M. Smits, 1968, Electrical conductivities in oil-bearing shaly sands: *Soc. Pet. Eng. J., Trans. AIME*, 243, 107-222.

Whitman, R. V., 1966, Miscellaneous studies of the formation of wave fronts in sand: Massachusetts Institute of Technology Dept. of Civil Engineering Research Report, R66-32.

Wilt, M., H. F. Morrison, A. Becker, H.-W. Tseng, K. Lee, C. Torres-Verdin, and D. Alumbaugh, 1995a, Crosshole electromagnetic tomography: A new technology for oil field characterization: *The Leading Edge*, 14, 173-177.

Wilt, M. J., D. L. Alumbaugh, H. F. Morrison, A. Becker, K. H. Lee, and M. Deszcz-Pan, 1995b, Crosswell electromagnetic tomography: System design considerations and field results: *Geophysics*, 60, 871-885.

Wyllie, M. R. J., A. R. Gregory, and L. W. Gardner, 1956, Elastic wave velocities in heterogeneous and porous media: *Geophysics*, 21, 41-70.

Wyllie, M. R. J., A. R. Gregory, and G. H. F. Gardner, 1958, An experimental investigation of factors affecting elastic wave velocities in porous media: *Geophysics*, 23, 459-493.

Progress Report

Surface and Borehole Electromagnetic Imaging of Conducting Contaminant Plumes

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Research Objective

Electromagnetic induction tomography is a promising new tool for imaging electrical conductivity variations in the earth (Wilt *et al.*, 1995a,b). The objective of this project is to join theory and experiment to produce enhanced tomographic images of electrically conducting fluids underground, allowing better localization of contaminants and improved planning strategies for the subsequent remediation efforts. The EM source field is produced by induction coil (magnetic dipole) transmitters deployed at the surface or in boreholes. Vertical and horizontal component magnetic field detectors are deployed in other boreholes or on the surface. Sources and receivers are typically deployed in a configuration surrounding the region of interest. The goal of this procedure is to image electrical conductivity variations in the earth, much as x-ray tomography is used to image density variations through cross-sections of the body. Although such EM field techniques have been developed and applied, the algorithms for inverting the magnetic data to produce the desired images of electrical conductivity have not kept pace. One of the main reasons for the lag in the algorithm development has been the fact that the magnetic induction problem is inherently three dimensional; other imaging methods such as x-ray and seismic can make use of two-dimensional approximations that are not too far from reality, but we do not have this luxury in EM induction tomography. In addition, previous field experiments were conducted at controlled test sites that typically do not have much external noise or extensive surface clutter problems often associated with environmental sites. To use the same field techniques in environments more typical of cleanup sites requires a new set of data processing tools to remove the effects of both noise and clutter.

Research Statement

The source field for induction tomography is a magnetic field generated by currents in wire coils. This field is normally produced in one borehole, while the received signals are the measured small changes in magnetic field in another, distant borehole; however, the method may also be used successfully in combination with surface sources and receivers. The goal of this procedure is to image electrical conductivity variations in the earth, much as x-ray tomography is used to image density variations through cross-sections of the body. Although field techniques have been developed and applied to the collection of such EM data, the algorithms for inverting the magnetic data to produce the desired images of electrical conductivity have not kept pace. The current state of the art in electromagnetic data inversion (Alumbaugh and Morrison, 1995a,b) is based on the Born/Rytov approximation (requiring a low contrast assumption), even though it is known that conductivity variations range over several orders of magnitude and therefore require nonlinear analysis.

Electromagnetic induction logging has long been used in the petroleum and environmental business to measure the electrical conductivity in the region immediately surrounding the borehole. This data, which is used to estimate pore fluid saturations near the well, is very sensitive to variations in rock pore fluid. Mapping surface variation of conductivity has also been found to be a very sensitive indicator of zones of higher salinity and acidity in many shallow environmental studies.

Recent research at LLNL (Newmark and Wilt, 1992; Wilt and Schenkel, 1992; Tseng *et al.*, 1995; Berryman, 1997) has developed instrumentation and software to deploy EM induction technology in crosshole and surface-to-borehole configurations, thereby extending the conductivity information to the region between boreholes. This results in a

determination of subsurface conductivity at a much higher resolution than can be achieved with surface techniques and much greater penetration than can be achieved with radar technology.

Although other technologies, such as ERT (Berryman and Kohn, 1990; Daily *et al.*, 1992; Ramirez *et al.*, 1993; Borcea, 1996; Borcea *et al.*, 1996), can produce electrical conductivity images at a useful spatial scale, the advantage of the electromagnetic induction technology is that we can make use of existing monitoring wells and the surface to do imaging. Since signals are transmitted and received inductively, we do not need to make ground contact (no ground penetrating electrodes); the technology is therefore relatively noninvasive. There is also the important potential advantage that multiple frequencies can be employed to improve the imaging capability for electromagnetic induction tomography; this feature is simply not available with ERT imaging since the inversion methods used are inherently based on the DC (zero frequency) limit of the pertinent equations.

We have had good success deploying the EM induction technology in petroleum applications for field characterization and steam flood monitoring, but it has yet to be used in noisy urban areas where we are often unable to drill holes or do anything invasive. The targets for imaging in environmental problems are significantly more variable than in the petroleum production environment, ranging from highly resistive DNAPLs and petroleum products to highly conducting acidic brines. Given this summary of the current state of electrical induction tomography, we now present our work in FY'97 to optimize this technology.

Research Progress

In this section, we summarize the progress made in the first year: (1) on code development and (2) on field tests of these methods. We conclude with a brief statement of the research directions for the second year of the project.

First Year Code-Development Effort

The summary presented in this section describes collaborative work done by Nathan J. Champagne II, J. Brian Grant, Robert M. Sharpe, H. Michael Buettner, and James G. Berryman, all of the Lawrence Livermore National Laboratory.

Forward Modeling

Since the transmitters in our field experiments are induction coils with alternating current at a fixed frequency (typically in the range 1-10 kHz), our basic numerical problem is to solve Maxwell's equations in the frequency domain. Because of the practical frequency range (< 1 MHz), it is adequate to ignore displacement currents in the formulation as is typically done by other researchers, but it is not essential to do so in the particular implementation that we have chosen. We have used the finite-difference frequency-domain formulation of Beilenhoff *et al.* (1992) and the anisotropic PML (perfectly matched layer) approach (Berenger, 1994) to boundary conditions of Wu *et al.* (1997) to deal with the fact that the computations must be done in a finite domain even though the real problem is effectively of infinite domain. The resulting formulas for the forward solver reduce to a problem of the form

$$\mathbf{Ax} = \mathbf{y},$$

(1)

where A is a non-Hermitian matrix with real values off the diagonal and complex values along its diagonal (Smith, 1996a,b). The matrix A may be either symmetric or nonsymmetric depending on details of the boundary conditions chosen (*i.e.*, the particular PML used in the application). Equation (1) must be solved for the vector x (which represents field quantities such as electric and magnetic fields) with the vector y determined by the boundary conditions and transmitter location. There are many choices of forward solver for this system [see for example Saad (1996)], but not many of these have been thoroughly tested for the type of matrix encountered in our problem. We found the stability characteristics of the standard Bi-CG algorithm for solving (1) to be quite inadequate (in terms of reliability and uniform accuracy) for this application and have chosen to use an alternative developed for such situations by van der Vorst (1992) called Bi-CGSTAB. We have found the stability characteristics of this solver to be entirely adequate for our application.

Considerable effort was devoted to finding good test cases for validating our new 3-D EM code. The *Proceedings of the International Symposium of Three-Dimensional Electromagnetics* which took place on October 4-6, 1995 at Schlumberger-Doll Research, contained a useful test problem in the contribution by Zhdanov and Feng (1995) in which a 20m \times 10m \times 10m conducting body is buried in a resistive half-space and excited by a wire loop transmitter. Our new code produced good agreement with the results of Zhdanov and Feng, and also with that from an older code, EM3d, from the University of Utah.

Test Cases

To demonstrate the accuracy of the new code further, we have tested various cases against results found in the literature. One example is for receivers down a borehole in a layered medium with air above the free surface, a 60m thick layer with conductivity equal to 0.3 S/m, a 25m thick layer with conductivity equal to 0.016 S/m, and a 60m layer with conductivity equal to 0.2 S/m at the bottom of the model, with appropriately designed PML absorbing layers on all six sides of the domain. Relative permittivity of all three earth layers is constant and assumed to be equal to 10.0. The frequency of the excitation is $f = 1$ kHz with the transmitter located at the free surface with an offset of 5m from the borehole. The finite difference representation was chosen so the unit spacing in the earth model was 2.5m, with 50 cells \times 50 cells in the xy direction, and 10 layers of PML on all four sides. In the vertical direction, there were 68 cells in the earth model, 10 cells in the air above the free surface, and 10 more cells above and below for the PML layers. All PML cells are 10m thick in the directions away from the earth model. The overall problem is then approximately $70 \times 70 \times 100 = \sim 500,000$ cells. The computations were performed on a DEC Alpha 8400 Model 5/4400, and required approximately 2 hours of CPU time, including about 2000 iterations to achieve the desired convergence. This computation was serial and required about 500 MB of memory. In Figure 1, the results of the code calculations for the magnetic field magnitude and phase are compared to results for the same model obtained using the code EM1D based on a semianalytical formula for such layered models and developed by Ki-Ha Lee at LBNL. The observed agreement is excellent.

Figure 1: Comparison of computed magnitude and phase of magnetic field in a layered model to semianalytic results of Ki-Ha Lee (LBNL).

The new code is written in Fortran 90 and is designed to be easily parallelizable, but we have not yet tested this feature of the code. We anticipate an improvement in execution time when the parallel features are invoked, but otherwise we expect the performance to be the same on the same computer platform.

First Year Field-Test Effort

The summary presented in this section describes collaborative work done by H. Michael Buettner, Clifford Shenkel, and Michael J. Wilt.

Experimental, field, and related work

Planning took place to improve the EM data acquisition system. Improvements include: 1) additional data channels, 2) faster, more reliable software, 3) purchase and testing of 3 new magnetometers for hole-to-surface imaging work, 4) securing a larger, newer, more reliable, safer data acquisition vehicle, and 5) a larger, newer, more reliable, safer boom/logging truck. The new system should allow us to collect better quality data more rapidly and reliably. Items 1, 3, 4, and 5 have been accomplished. Item 2 is still in progress.

Experimental work at Lost Hills, CA

During the week of April 7, 1997, we collected borehole to surface EM data for a shallow steam injection which is underway at Mobil Oil's Lost Hills-3 field. This is an interesting case because it can be viewed as an analog of a shallow environmental remediation using steam injection. Surface magnetic field data (vertical and radial fields, magnitude and phase) were collected at 18 receiver stations along two profiles which ran radially from the EM transmitter well from 5m to 120m. The data at each surface station were collected while the EM transmitter was raised slowly from a depth of 120m to a final depth of 20m. As part of this experiment, a calibration of the EM transmitter was also performed.

The data from this experiment have not been analyzed as yet, primarily because good interpretation tools are not available. Some simple 1-D modeling was done to confirm that the expected conductivity change in the steam zone should produce an anomaly large enough to detect in the measured data when comparing the pre-steam to the post-steam conditions.

During this effort, we worked on the problem of removing cultural effects (*e.g.*, fences, pipes, etc.) from EM data. This involved a survey of the literature and discussions with M. Wilt and W. Daily. The only approach found thus far involves spatial filtering of the raw

magnetic field data. That is, the rapid spatial variations need to be filtered out before interpretation begins.

Directions of Research in the Second Year of the Project

We will continue to test and improve the forward modeling capability developed in the first year of the project. At the same time a new approach to the inverse problem of electromagnetics is being developed based on the so-called "adjoint technique." This method has the very useful property that the inverse problem can be solved approximately by making two uses of the same forward modeling code we have already developed. The updates to the electrical conductivity will be obtained by first making one pass through the code using the latest best guess of the nature of the conducting medium, and then another pass with the adjoint operator (which for this problem is just the conjugate transpose of the operator A). Then the results of the two calculations are combined to determine the first update to the original conductivity model. This process is repeated until the desired degree of convergence is achieved.

Fields tests are planned for the second year as well. There is one field site at present which may present a good opportunity for field testing our system. That site is the Southern California Edison pole yard at Visalia, CA, which is contaminated with creosote. The site is currently under steam remediation and is being monitored using ERT (electrical resistance tomography). Other sites may become available as well.

EM induction data were collected at the LLNL main site recently by a group from UC Berkeley, and these data are available to us. This is not an active remediation site, but it does have some of the elements of interest to us. For example, it has some organic contamination, soils typical of the Western United States, and monitoring wells for both EM induction and ERT.

We would also like to conduct a calibration for our EM transmitter coils at a highly-resistive site if such a site can be found where the experiment can be done for a reasonable cost.

Cited References

Alumbaugh, D. L., and H. F. Morrison, 1995a, Monitoring subsurface changes over time with cross-well electromagnetic tomography, *Geophysical Prospecting* **43**, 873-902.

Alumbaugh, D. L., and H. F. Morrison, 1995b, Theoretical and practical considerations for crosswell electromagnetic tomography assuming cylindrical geometry, *Geophysics* **60**, 846-870.

Beilenhoff, K., W. Heinrich, and H. L. Hartnagel, 1992, Improved finite-difference formulation in frequency domain for three-dimensional scattering problems, *IEEE Trans. Microwave Theory Tech.* **40**, 540-546.

Berenger, J. P., 1994, A perfectly matched layer for the absorption of electromagnetic waves, *J. Computational Phys.* **114**, 185-200.

Berryman, J. G., 1997, Challenges for computational physics in underground imaging of electrically conducting contaminant plumes, invited talk P2.03 in special session on Geological Phenomena at the *International Conference on Computational Physics*,

American Physical Society, Division of Computational Physics, Santa Cruz, California, August 25-29, 1997.

Berryman, J. G., and R. V. Kohn, 1990, Variational constraints for electrical impedance tomography, *Phys. Rev. Lett.* **65**, 325-328.

Borcea, L., 1996, *Direct and Inverse Problems for Transport in High Contrast Media*, Ph.D. thesis, Stanford University, May, 1996.

Borcea, L., J. G. Berryman, and G. C. Papanicolaou, 1996, High contrast impedance tomography, *Inverse Problems* **12**, 835-858.

Daily, W. D., A. Ramirez, D. LaBrecque, and J. Nitao, 1992, Electrical resistivity tomography of vadose water movement, *Water Resources Res.* **28**, 1429-1442.

Kuzuoglu, M., and R. Mittra, 1996, Frequency dependence of the constitutive parameters of causal perfectly matched anisotropic absorbers, *IEEE Microwave Guided Wave Lett.* **6**, 447-449.

Newmark, R. L., and M. J. Wilt, 1992, Monitoring underground steam injection using geophysical logs, in *Dynamic Underground Stripping Demonstration Project -- Interim Engineering Report*, edited by R. L. Newmark, LLNL UCRL-ID-110064, April, 1992, pp. 343-372.

Ramirez, A., W. D. Daily, D. LaBrecque, E. Owen, and D. Chesnut, 1993, Monitoring an underground steam injection process using electrical resistance tomography, *Water Resources Res.* **29**, 73-87.

Saad, Y., 1996, *Iterative Methods for Sparse Linear Systems*, PWS Publishing, Boston.

Smith, J. T., 1996a, Conservative modeling of 3-D electromagnetic fields: Part I. Properties and error analysis, *Geophysics* **61**, 1308-1318.

Smith, J. T., 1996b, Conservative modeling of 3-D electromagnetic fields: Part II. Biconjugate gradient solution and an accelerator, *Geophysics* **61**, 1319-1324.

Tseng, H.W., A. Becker, and M. J. Wilt, 1995, A borehole-to-surface electromagnetic survey, *Society of Exploration Geophysicists Expanded Abstracts*, Proceedings of the International Exposition and Sixty-Fifth Annual Meeting, Houston, Texas, October 8-13, 1995, pp. 246-249.

van der Vorst, H. A., 1992, Bi-CGSTAB: A fast and smoothly converging variant of Bi-CG for the solution of non-symmetric linear systems, *SIAM J. Sci. Stat. Comput.* **12**, 631-644.

Wilt, W. J., D. L. Alumbaugh, H. F. Morrison, A. Becker, K. H. Lee, and M. Deszcz-Pan, 1995a, Crosswell electromagnetic tomography: System design considerations and field results, *Geophysics* **60**, 871-885.

Wilt, M., H. F. Morrison, A. Becker, H.-W. Tseng, K. H. Kee, C. Torres-Verdin, and D. Alumbaugh, 1995b, Crosshole electromagnetic tomography: A new technology for oil field characterization, *The Leading Edge* **14**, March, 1995, pp. 173-177.

Wilt, M. J., and C. Schenkel, 1992, Cross-borehole electromagnetic induction at the Dynamic Underground Stripping clean site, in *Dynamic Underground Stripping Demonstration Project -- Interim Engineering Report*, edited by R. L. Newmark, LLNL UCRL-ID-110064, April, 1992, pp. 407-425.

Wu, J. Y., D. M. Kingsland, J. F. Lee, and R. Lee, 1997, A comparison of anisotropic PML to Berenger's PML and its application to the finite-element method for EM scattering, *IEEE Trans. Antennas Prop.* **45**, 40-50.

Zhdanov, M. S., and S. Feng, 1995, Quasi-linear approximation in 3D electromagnetic modeling, in *Proceedings of the International Symposium of Three-Dimensional Electromagnetics*, October 4-6, 1995, Schlumberger-Doll Research, Ridgefield, Connecticut, edited by M. Oristaglio and B. Spies, pp. 251-257.

Summary of Accomplishments

- * A new 3-D imaging code was found to be in good agreement with an older code running a reference problem as well as with results found in the literature. The new code is written in Fortran90 and, therefore, is easily converted for use on parallel computing platforms.
- * Our EM data-acquisition system was substantially improved including the addition of more data channels, the purchase and testing of 3 new magnetometers for hole-to-surface imaging work, the securing of a larger, newer, more reliable, safer data acquisition vehicle, and a larger, newer, more reliable, safer boom/logging truck.
- * We collected a new borehole to surface EM data set for a shallow steam injection which is underway at Mobil Oil's Lost Hills-3 field. Some simple 1-D modeling was done to confirm that the expected conductivity change in the steam zone should produce an anomaly large enough to detect in the measured data when comparing the pre-steam to the post-steam conditions.
- * A new algorithm has been developed for inverting the electromagnetic field data for electrical conductivity distribution. The new algorithm uses an adjoint technique similar to ones that have been used extensively in other very large computational problems in geophysics such as reflection seismology.

